Sunday Afternoon, October 18, 2015

Biomaterials Plenary Session
Room: 211D - Session BP-SuA

Biomaterials Plenary Session
Moderator: Graham Leggett, University of Sheffield

3:00pm **BP-SuA1 Phage, Peptides and Polymers: Targeted Polymeric Delivery using Peptide Ligands Identified by Phage Display**, *L. Chan, M. Cieslewicz, G. Liu, B. Livesay, C. Ngambenjawong,* ***Suzie Pun****, S. Salipante, N. White*, University of Washington **INVITED**

Peptide phage display is a powerful tool for identifying novel targeting ligands. We have recently used peptide phage display combined with next generation sequencing for efficient identification of targeting ligands. I will first present our discovery of a peptide that preferentially binds to "anti-inflammatory" (M2) macrophage. This peptide can be used to target tumor-associated, M2-like macrophage in the tumor microenvironment. Multivalent display of this peptide using peptide-based copolymers significantly increases binding avidity of the polymer with M2 cells. In a second example, a fibrin-binding peptide identified by the Caravan Group (Massachusetts General Hospital) using peptide phage display was incorporated into brush-shaped, peptide-based copolymers. These polymers were synthesized by controlled radical polymerization with well-defined compositions and molecular weights and possess the biological functions contributed by their peptide components. The resulting polymer incorporates into forming clots and increases clot strength while improving resistance to clot lysis. Delivery of this polymer to a rat model of trauma significantly improved survival compared to controls.

3:40pm **BP-SuA3 Experimental and Theoretical Challenges regarding the Fundamental Interactions between Biomolecules and Biosurfaces**, ***Jacob Israelachvili***, University of California at Santa Barbara **INVITED**

I will try to consider some key fundamental questions and challenges in the interactions of biomolecules and biosurfaces – what important interactions we still don't understand, what is known but is subtle and often misunderstood, and current experimental and theoretical limitations that need to be overcome – all with examples to illustrate the points being made.

The hydrophobic interaction is one of the most important for determining biomolecular organization (of membranes, proteins) but is still not understood both at the experimental and theoretical levels; for example, there is still no generally accepted "interaction potential" or "force law" for this interaction, although it appears to be an exponential functions of the separation between surfaces (but as yet totally unknown between molecules or hydrophobic groups).

Perhaps more importantly for biological interactions, given that living systems are never at rest, or at thermodynamic equilibrium, or even necessarily tending toward the equilibrium state, the issue of non-equilibrium interactions is still a very dark area. I am not referring here to viscous forces, but to interaction potentials that are *inherently* rate or time-dependent. Some ligand-receptor binding and unbinding interactions present good examples of such "dynamic" interactions.

A very commonly misunderstood feature in the area of bioadhesion is the difference between strong and weak bonds, or high adhesion and low adhesion. Without specifying whether one is talking about the energy or the force, any comparisons can be meaningless. Examples will be given of real situations where the same change in energy can result in 8 orders of magnitude difference in the forces (pressures or stresses) depending on the geometry, i.e., structure and mechanical properties of the adhering (bio)material surfaces. There are also many practical situations where friction and adhesion forces are involved simultaneously, for example, when geckos run on walls and ceilings, giving rise to very subtle effects.

Experimental and theoretical (e.g., simulation) challenges involving complex biological interactions will also be discussed: these involve 'scaling effects of *size*' (converting the interactions of single or a few molecules or bonds to those between biological surfaces that involve the correlated interactions of many molecules or bonds, usually at different locations), and 'scaling effects of *time*' where the time scales of a biological process involving multiple (sequential) interactions that evolve both in space and time over large distances and long times are currently inaccessible by computers.

4:20pm **BP-SuA5 Biomimetic Surface Coatings Inspired by Polyphenols Found in Mussels, Tea, Wine and Chocolate**, *T. Sileika, D. Barrett,* Northwestern University, ***Phillip Messersmith***, University of California at Berkeley **INVITED**

Polyphenols are found in both plant and animal tissues, where they serve a variety of functions including mechanical adhesion, structural support, pigmentation, radiation protection, and chemical defense. In animals, polyphenols are found in the adhesive proteins secreted by sessile marine organisms. In mussels, the adhesive proteins are known to contain high levels of 3,4-dihydroxy-L-alanine (DOPA), an amino acid that is believed to be important in adhesion to substrates. In plants, polyphenolic compounds containing benzenediol (catechol) and/or benzenetriol (gallol) functional groups are widely distributed secondary metabolites with a variety of biochemical and physical functions. Consumption of foods and beverages rich in polyphenols are claimed to be beneficial to one's health.

This talk will focus on selected biological polyphenols that are rich in catechol or gallol functional groups, with the goal of developing novel materials inspired by biological polyphenols. In the case of mussel-inspired biomaterials, we focus on understanding the molecular aspects of mussel adhesion, and in developing biomimetic polymer hydrogels and coatings from synthetic catechol containing polymers[1-4]. These biologically inspired materials have a variety of functional uses, including tissue repair, drug delivery and antifouling coatings. In the case of plant polyphenols, we as well as others have recently discovered that gallol-rich compounds found in tea, coffee beans, cacao beans and other plant tissues form thin adherent polymerized films on substrates by simple immersion [5,6]. Deposition is facile on a variety of solid, porous and nanoparticulate substrates composed of metals, ceramics and polymers. In addition to possessing inherent antibacterial and antioxidant properties, the nanoscale polyphenol films serve as versatile 'primers' facilitating secondary modifications of the primer coating such as metallization and covalent grafting of biomolecules and synthetic polymers. Such secondary modifications can be exploited for a variety of practical applications, including antibacterial, antioxidant and fouling resistant coatings on medical devices, metal deposition, plasmonic tuning and surface functionalization of nanoparticles.

References

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6. Sileika, T.S., et al., Angew Chem Int Ed Engl, 2013. 52: 10766.

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 MoS_2**, ***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 ^{o}C. 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.

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[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.

Work supported by the Center for Low Energy Systems Technology (LEAST), one of six SRC STARnet Centers sponsored by MARCO and DARPA, and by NSF-EFRI-1433496.

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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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].

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Applied Surface Science
Room: 212D - Session AS-MoM

Quantitative Surface Analysis: Obtaining Quantitative Information in the Face of Material Complexity and Morphology Influences

Moderator: Christopher Szakal, National Institute of Standards and Technology (NIST), Alberto Herrera-Gomez, CINVESTAV-Queretaro, Mexico

8:20am **AS-MoM1 Quantitative XPS of Core-Shell Nanoparticles**, ***Cedric Powell***, National Institute of Standards and Technology (NIST), *M. Chudzicki, W.S.M. Werner, W. Smekal*, Technical University of Vienna, Austria

We used the new version of the NIST Database for the Simulation of Electron Spectra for Surface Analysis (SESSA) [1] to simulate XPS spectra of core-shell nanoparticles (NPs). Two series of simulations have been made. First, Cu 2p spectra were simulated using Al Kα x-rays for a monolayer of three types of Cu-Au NPs on an Si substrate: (a) an Au shell of variable thickness on a Cu core with diameters of 0.5 nm, 1.0 nm, 2.0 nm, 5.0 nm, and 10.0 nm; (b) a Cu shell of variable thickness on an Au core with diameters of 0.5 nm, 1.0 nm, 2.0 nm, 5.0 nm, and 10.0 nm; and (c) an Au shell of variable thickness on a 1 nm Cu shell on an Au core with diameters of 0.5 nm, 1.0 nm, 2.0 nm, 5.0 nm, and 10.0 nm. For these three morphologies, the outer-shell thickness was varied until the Cu $2p_{3/2}$ peak intensity was the same (within 2 %) as that found in our previous work with planar Cu/Au morphologies [2]. For each morphology, we performed simulations with elastic scattering switched on and off. We found that elastic-scattering effects were generally strong for the Cu-core/Au-shell and weak for the Au-core/Cu-shell NPs; intermediate elastic-scattering effects were found for the Au-core/Cu-shell/Au-shell NPs. The shell thicknesses required to give the selected Cu $2p_{3/2}$ peak intensity for the core-shell NPs were less than the corresponding film thicknesses of planar samples since Cu 2p photoelectrons can be detected from the sides and, for the smaller NPs, bottoms of the NPs.

Second, we determined effective attenuation lengths (EALs) for Cu $2p_{3/2}$ photoelectrons from NPs consisting of a Cu core of diameters 0.5 nm, 1 nm, 2 nm, 5 nm, and 10 nm and a Cu shell with thicknesses between 0.25 nm and 3.75 nm. The EAL was determined from the Cu $2p_{3/2}$ intensity from the core with no shell and from the Cu $2p_{3/2}$ intensity from the core that was attenuated by a Cu shell of specified thickness. These EALs varied systematically with both Cu-core diameter and Cu-shell thickness. While the inelastic mean free path of Cu $2p_{3/2}$ photoelectrons (at 534 eV) in Cu is 1.12 nm, the EALs for a 10 nm Cu core varied from 0.53 nm to 0.65 nm as the Cu-shell thickness increased from 0.25 nm to 3.75 nm. In contrast, the EALs for a 0.5 nm Cu core increased from 0.78 nm at a shell thickness of 0.25 nm to a maximum value of 0.86 nm for a shell thickness of 0.75 nm and then decreased to 0.81 nm for a shell thickness of 3.75 nm. These changes show the important roles of NP morphology, NP dimensions, and elastic scattering in determining shell thicknesses by XPS.

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8:40am **AS-MoM2 The Satellites of the 2*p* Core Level of Transition-Metals**, ***Alberto Herrera-Gomez***, CINVESTAV-Queretaro, Mexico

The shake-up satellites in XPS spectra are due to intrinsic energy losses as the photoelectron leaves the hosting atom. The first row transition metals, either in the metallic or in the oxide form (and sometimes in both), display clear shake-up features in the corresponding 2*p* core level. They are difficult to quantify because the shape of the main 2*p* peaks of these elements are highly asymmetric and the spectra contains a large background contribution. In fact, there is a frequent correlation between the presence of satellites and a large background intensity and, also, a large peak shape asymmetry. Through newly developed procedures it has been possible to properly fit all these core levels. In addition to those already described in the literature, the procedures allowed for pinpointing previously unreported shake-up satellites. A common feature of the satellites is that their spin-orbit splitting exhibits a remarkable difference with the associated to the main peak, suggesting angular-dependent correlation effects.

9:00am **AS-MoM3 Quantitative Analysis of Advanced Commercial Glasses for Display Technologies**, ***Cody Cushman,*** Brigham Young University, *N.J. Smith,* Corning, *T. Grehl, P. Bruener,* ION-TOF GmbH, Germany, *M.R. Linford*, Brigham Young University

A series of complex, multicomponent commercial glasses used in advanced display applications was exhaustively analyzed by X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), low energy ion scattering (LEIS), Rutherford backscattering (RBS), atomic force microscopy (AFM), and spectroscopic ellipsometry, where the purpose of this study was to quantify the compositions and properties of these materials. XPS revealed the compositions of the upper ca. 10 nm of the glasses, which differed substantially from each other. Angle resolved XPS suggested some segregation of some elements to the surfaces. These results were confirmed by LEIS, which conclusively identified the elements at the true surfaces of the materials in a quantitative fashion. Like XPS, ToF-SIMS probed the near surface regions of the materials. However, it also identified elements that were beyond the detection limit of XPS. In addition, ToF-SIMS was used with XPS to quantitatively determine the concentration of –OH groups at the surfaces of the glasses via the $SiOH^+/Si^+$ ratio. Atomic force microscopy (AFM) showed that the materials were all extremely flat, with roughnesses on the order of 1 nm. Spectroscopic ellipsometry from 200 – 1700 nm was used to determine the optical properties (quantitative dispersion relationships) of the glasses. These techniques provided a comprehensive analysis of these glass samples. In addition, the glasses were subjected to various cleaning procedures (plasma, wet chemical cleans, etc.) and other surface treatments. The same suite of analytical techniques was then used to show conditions that led to changes or no changes in the compositions of the glasses, and these changes were quantified.

9:20am **AS-MoM4 New Horizons in Practical Applications of Sputter Depth Profiling**, *W.F. Stickle, C.N. Young, M.D. Johnson,* HP*, A.A. Ellsworth,* ***Amy Walker***, University of Texas at Dallas

In the application of x-ray photoelectron spectroscopy the use of sputter depth profiling is one of the routinely used methods for analysis. Most industrial laboratories study a wide variety of material systems such as polymers or inorganic thin films and many of these material systems require analysis not just of the as received surface, but also of and through the depth of a thin film. Historically, mono atomic argon has been the ion source of choice in XPS, but even at low ion energies mono atomic argon will damage not only polymer systems converting them into amorphous carbon but also damage inorganic materials by creating, for example, intermediate oxides. In recent years other ion sources have become routinely available such as $C60^+$ and most recently, gas cluster ion sources. From a practical standpoint, i t is important to understand the sputter induced chemistry that may be created by these various sources and the trade-offs for applying these different primary ion sources for routine surface chemical analyses. The effects of preferential sputtering and chemical changes or reactions of metal oxides will be discussed. Several different material systems are examined and discussed by comparing the information obtained using mono atomic argon, an argon gas cluster source and a $C60^+$ ion gun for enhancing and clarifying 'routine' analyses. The different types of samples to be discussed will include niobium oxides, titanium nitride and multilayer thin films.

9:40am **AS-MoM5 ASSD 30th Anniversary Lecture: Sensitivity Factors in XPS: Where Do They Come From and How Accurate Are They?**, ***John Grant***, University of Dayton **INVITED**

The most common method for quantitative analysis in X-ray Photoelectron Spectroscopy (XPS) incorporates relative sensitivity factors. In the 1970s and 1980s, several research groups studied the relative intensities of photoelectron lines and attempted to generate tables of relative sensitivity factors. Calculations were also made of ionization cross-sections using Mg and Al Kα x-rays, and experimental measurements were often compared to theory. The seminal measurements were made by Wagner and co-workers, who used two different types of electron energy analyzers from two different manufacturers and compared the results with theory and with other measurements. They found that the agreement in data from the two instruments on the same compounds was good, and they generated a table of empirically derived sensitivity factors. Today, many XPS analysts still use the relative sensitivity factors from Wagner's work, particularly if they use an instrument where the sensitivity factors were not provided. An early ASTM round-robin on XPS measurements on catalysts by 12 laboratories found a large spread in measured peak intensity ratios, even for instruments of the same manufacture, concluding that a calibration procedure for the intensity response of instruments was needed. A later ASTM round-robin on pure Au and Cu concluded that the spread in intensity ratios was typically a factor of ten. Based on these results, Seah spearheaded studies on instrument transmission functions and developed a method so that the relative instrument response function between two different analyzers was better than 5%. In 1990, he published standard reference spectra for XPS and claimed all instruments may be calibrated absolutely to an accuracy of ± 2%. The National Physical Laboratory (NPL) developed and sold a procedure for generating an instrument transmission function, but it was not widely adopted. At least one manufacturer developed a model for measuring the transmission function in their instruments and measures it on each instrument before shipping it to the purchaser. A digital database of spectra was also developed at NPL, and could have provided a set of relative sensitivity factors for XPS, but it was never sold. It is important to know the origin of the sensitivity factors supplied by manufacturers and any limits placed on their applicability. By measuring spectra from a number of reference compounds one can quickly learn how reliable they are. For the most accurate measurements, one should measure relative sensitivity factors from standard compounds that match as closely as possible the compositions of unknowns.

10:40am **AS-MoM8 Ar^+ and Cluster Ion Depth Profiling for Quantitative XPS Inorganic Thin Film Analysis**, ***Jennifer Mann**, J.F. Moulder, S.R. Bryan, J.S. Hammond*, Physical Electronics

A successful XPS sputter depth profile should accurately identify layer thickness and composition of materials as a function of depth within film structures. In the case of inorganic thin films, monoatomic argon ion beam depth profiling continues to be the preferred choice despite issues with preferential sputtering, material migration, and chemical reduction that may occur during the sputter process to alter the apparent profile of the analyzed material [1-3].

The introduction of C_{60} cluster ion beam and argon gas cluster ion beam (GCIB) sputtering in recent years provided the capability of successful depth profiling of polymer and organic materials as well as thin film structures while preserving the stoichiometry and chemical structures [4,5].

Currently, there is great interest in establishing the viability of these cluster ion sources as an alternative to Ar^+ ion beam sources for analyzing inorganic semiconductor and glass films, with particular interest in a possible improvement in the quantitative accuracy of the depth profile results compared to Ar^+ depth profiling [6,7].

The XPS depth profile of a thin film of the semiconductor material Indium Gallium Zinc Oxide (IGZO) was acquired with Ar^+, C_{60}^+ and GCIB ion guns. The film thickness and composition was characterized by RBS. Preferential sputtering of the In through the thin film depth profiles was observed with all three ion sources. The highest level of preferential sputtering of In was observed with the Ar^+ source while the C_{60}^+ source produced a relatively constant composition through the depth profiles and the most consistent with the expected elemental composition. The sputter volume per incident ion, the resulting interface width and the sputter crater roughness for the three different ion sources was also evaluated.

Similar evaluations for additional thin film oxide samples will also be presented. The results for these comparative studies suggest that depending on the composition of the inorganic oxide thin films, cluster ion sources may provide superior quantitative depth profiling for inorganic oxide thin film samples as well as organic thin film samples.

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11:00am **AS-MoM9 Preservation of Chemical States in Mixed Material Surfaces when Profiling with Noble Gas Clusters**, ***Christopher Deeks**, J.P.W. Treacy, P. Mack, T.S. Nunney*, Thermo Fisher Scientific, UK

The technique of X-ray Photoelectron Spectroscopy (XPS) is valued within the surface science community because it offers chemical quantification combined with surface specificity. The inherent surface sensitivity is due to the short mean free path of electrons (several nanometres) within solid media. Deducing the chemical composition of layers and interfaces at greater depths is achieved through milling the topmost layers by bombardment with argon ions. It has been well established, however, that milling with monatomic argon ions can cause sputter-induced damage at the surface, which in turn leads to a loss of chemical state information.

Surface etching with large clusters of argon enables the rapid collection of depth profiles from organic materials and removal of contamination from metal oxides while maintaining the chemical character of a material. Due to the relatively low energy per atom, however, the etch rates of most inorganic materials with these large clusters is not conducive to a high sample throughput. The implementation of smaller gas clusters allows higher energies per atom to be used, leading to increased rates of etching whilst preserving the chemical information that is lost when using monatomic argon.

Here we shall discuss how using a wider range of *ion energies per atom* enables more effective depth profiling of a wide variety of surface materials. We will present data from mixed inorganic and organic samples to show the benefits of these reduced cluster sizes.

11:20am **AS-MoM10 Photoemission from Complex Material Systems: Obtaining Quantitative Information**, ***Robert Opila**, J. Church*, University of Delaware **INVITED**

Photoemission is still a rapidly developing technique for surface analysis of complex systems using advancing physical and software technologies. In this talk we will consider two applications of electron spectroscopy taking advantage of hardware and software innovations.

Recently, the adaptation of XPS studies to synchrotron beamlines has produced a new technique – Variable Kinetic Energy XPS (VKE-XPS). VKE-XPS collects XPS data at multiple photon energies, and by doing so, also varies the likelihood of detection of electrons from buried layers. Compositional depth information can be extracted from VKE-XPS data sets by statistically sifting through the data using likelihood calculations assigned to each randomly generated depth profile. We have deployed a new algorithm, Bayes-Sim, which applies a Bayesian statistical approach to establish the framework for a belief system for each compositional simulation. Optimization of the search is carried out using a simulated annealing schedule, which assists in avoiding only locally optimized configurations. The Bayes-Sim algorithm has been encapsulated in a distributable, open-source graphical user interface J-FAB. These improvements were used to study high dielectric materials

Some of the most advanced chemical analytical techniques have been applied to study the degradation of paint pigments from artists in the post-impressionist era (late to early 20th century). The capability to investigate chemical speciation and elemental mapping in micro-samples is enabled only by the spatial resolution and high brilliance of synchrotron techniques like XANES and SR-FTIR. Fairly sophisticated data analyses for synchrotron beam lines have been encapsulated in easy to use software packages thereby complimenting the burgeoning field of art in science with the tools needed to tackle complex problems. In this work degradation of paintings by Munch and Matisse will be discussed.

Biomaterial Interfaces
Room: 211D - Session BI+AS-MoM

Characterization of Biological and Biomaterials Surfaces (1)

Moderator: Dan Graham, University of Washington, Joe Baio, Oregon State University

8:20am **BI+AS-MoM1 Characterizing the Dissociative Properties of Surface-Bound Biomolecules by *In Vacuo* XPS**, ***Kenan Fears***, Naval Research Laboratory

In vacuo X-ray photoelectron spectroscopy (XPS) was used to determine the dissociation constant for pH-tunable, peptide nanostructures on a gold substrate. To validate these protocols, dissociation constants of GG–X–GG and X_5 peptides (X = G, D, H, or K), and bovine albumin (BSA) and fibronectin (FN) were measured for comparison with published values. Drops of biomolecules in 100 mM sodium phosphate buffers (pH 1-12) were deposited on gold substrates and allowed to dry at room temperature. Due to the ca. +1.3 eV shift in binding energy (BE) of protonated amines, pK values of basic amino acids were calculated by plotting the fraction of protonated amines as a function of solution pH. Similarly, the BE of carboxyl groups shifted ca. -1.3 eV upon deprotonation. While C 1s spectra were convoluted by the multiple chemical states of carbon present in the samples, the ratio of the C 1s components centered at BE=289.0 ± 0.4 and BE=287.9 ± 0.3 proved to reliably assess deprotonation of carboxyl groups. The pK values for the Asp (3.1 & 2.4), His (6.7), and Lys (11.3 & 10.6) peptides, and the pI of BSA (4.8) and FN (5.7), were consistent with published values; thus, validating the pK value obtained for our surface-bound nanostructures using these methods.

9:00am **BI+AS-MoM3 Quantifying the Surface Chemistry and Overlayer Thickness of Functionalized Nanoparticles**, ***David Castner***, University of Washington **INVITED**

Nanoparticles exhibit unique surface properties and require well-controlled surface properties to achieve optimum performance in complex biological or physiological fluids. Despite the widespread appreciation of the unique properties of high surface area nanoparticles there is a surprising lack of detailed surface characterization of these materials, especially for nanoparticles used in biomedical applications. This is in part because nanoparticles present significant challenges for surface characterization. Thus, there is a need to develop rigorous and detailed surface analysis methods for characterizing the surface of nanoparticles. Model systems with well-defined, systematic variations of surface properties are an excellent starting point for developing comprehensive, multi-technique surface characterization methodologies. We have developed methods for quantifying the thickness and structure of carboxylic acid (COOH) SAM functionalized Au nanoparticles (AuNPs) using XPS, SESSA and LEIS. The size, shape, and size distribution of the AuNPs was determined by TEM. Additional surface properties were characterized using ToF-SIMS and FTIR spectroscopy.

These methods were then extended to the covalent attachment of proteins to AuNPs functionalized with OEG SAMs. For the OEG functionalized AuNPs the type of end group (OH vs. OCH_3) doesn't have a significant effect on the SAM thickness and structure, but the size of the AuNP does. The C11 alkyl portion of the thiol molecules was well ordered on all surfaces (flat, 14nm and 40nm). In contrast, the OEG portion of the thiol molecules was better ordered and more densely packed on the 40nm AuNPs compared to the 14nm AuNPs. LEIS measurements showed OEG SAMs had a thickness of 2.0 nm on the 14nm AuNPs compared to 2.6 nm on the 40nm AuNPs. Protein G was immobilized onto the HO-terminated OEG SAMs via carbonyl diimidazole chemistry. On flat Au surfaces XPS showed a monolayer of Protein G was covalently immobilized with little non-specific adsorption. On AuNPs a monolayer of Protein G could also be immobilized, but significant non-specific adsorption was detected.

Recent studies on NPs with Au cores and Ag shells have shown that it is important to account for non-spherical particle shapes of the Ag shell and off-center locations of the Au cores to obtain good agreement between the SESSA and XPS results. Both deviations from ideal core-shell spherical particles result in higher than expected XPS Au concentrations, with the off-center Au cores having the largest contribution to this effect for the particular core-shell NPs examined in this study.

9:40am **BI+AS-MoM5 Structure-Function Relation in Gizzard Plates of Cephalaspidean Gastropod**, *M. Shepelenko, V. Brumfeld, E. Klein,* Weizmann Institute of Science, Israel*, H. Lubinevsky,* Israel Oceanographic & Limnological Research (IOLR) and National Institute of Oceanography, *L. Addadi, S. Weiner,* ***Sidney Cohen***, Weizmann Institute of Science, Israel

Processing food is an essential function of all organisms. Although grinding of food is typically done by teeth, there are a number of species that perform this action in the muscular stomach or gizzard. This places unique demands on the food processing mechanism, a study of which provides fascinating insights into compositional, structural, and mechanical design of the organism at the nanoscale. The Cephalaspidean gastropods are common marine mollusks with a specialized digestive apparatus containing 3 hardened plates of millimeter size inside the gizzard. The gizzard plates are reported to either grind or crush shelled prey. In this study we apply a variety of techniques including micro-CT, scanning electron microscopy with energy dispersive x-ray spectroscopic analysis, infrared and Raman spectroscopies, powder x-ray diffraction and nanoindentation to understanding the manner in which the gizzard plates of the cephalaspid *Philine quadripartita* function in the overall digestion process. We determined that the gizzard plates, used to crush the shelled prey, have distinct structure and composition which promote optimal performance of their function. Specifically, the plate composition, a mixture of amorphous calcium carbonate and amorphous calcium phosphate embedded in a chitinous matrix, varies systematically with depth into the plate. The corresponding elastic moduli and hardness of the plates vary accordingly. In contrast to typical teeth, for which the surface comprises the stiffest and hardest material, the hardest and stiffest layer of the gizzard plates is below the working surface. Analysis of the elasticity index (H/E) of the gizzard plates, and comparison with sea urchin teeth, which we have extensively studied in the past, provided interesting insights into the connection between the biological function and mechanical properties of the gizzard plates. Sea urchin teeth, which serve a grinding function, exhibit higher wear resistance and stiffness than gizzard plates which are used for crushing. Nonetheless, the difference in toughness between the two, as determined by comparison of respective in elasticity indices, is relatively small.

10:00am **BI+AS-MoM6 Photothermal AFM-IR of Bacteria on Polymer Films: Impact of Cantilever Damping on Quantitative IR Measurements**, ***Daniel Barlow***, *J.C. Biffinger,* Naval Research Laboratory*, A.L. Cockrell,* Nova Research*, M. Lo, K. Kjoller, D. Cook,* Anasys Instruments*, W. Kyung Lee, P.E. Pehrsson,* Naval Research Laboratory*, W.J. Goodson,* Air Force Research Laboratory*, J.N. Russell, Jr.*, Naval Research Laboratory

Synthetic polymers can be prone to degradation in microbial and other biological environments, often through enzymatic activity. Quantitative assays are important to characterize these degradation mechanisms and accurately correlate relationships with environmentally dependent microbial physiology. For microbial degradation of polyurethane films, conventional FTIR microscopy has been previously applied in quantitative assays with micron – scale spatial resolution. Photothermal AFM-IR offers the potential to extend this analysis to the nanoscale, allowing early degradation processes and mechanisms relative to single microbes to be quantified. As a first step towards this, we have used AFM-IR to characterize a known polyurethane degrading microbe (*Pseudomonas fluorescens*, Pf01) grown on films of a polyether – polyurethane (PU) formulation known to resist enzymatic degradation. This allowed us to conduct preliminary AFM-IR assessments with a relevant microbe and polymer, but without additional complications from biodegradation. Height images of air-dry samples showed the growth procedure in liquid media resulted in monolayer Pf01 biofilm clusters on top of the ~250 nm PU layer, providing a conducive model system for AFM-IR in an ATR configuration. Both bacteria and PU spectral signatures were detectable by AFM-IR spectroscopy and showed generally good agreement with FTIR. However, PU AFM-IR absorption intensities were observed up to 2x higher in regions covered by dried bacteria, versus uncovered regions, even though the PU thickness was uniform over the substratum. This was due to damping variations which were reflected in the cantilever ring-down and attributed to differences in loss modulus and tip – sample adhesion for the two materials. This shows that local cantilever damping can be an important property to assess in AFM-IR analysis of combined biological / polymer samples, a factor that has received little attention thus far. Analysis of the cantilever ring-down will be discussed regarding extraction of damping parameters for normalization of the IR signal.

10:40am **BI+AS-MoM8 Where's Waldo? 3D Localization of Polymer Nanoparticles in Cells using ToF-SIMS**, ***Daniel Graham***, University of Washington, *J.T. Wilson*, Vanderbilt University, *J. Lai, L.J. Gamble, P.S. Stayton, D.G. Castner*, University of Washington

Polymeric nanoparticles have shown promise for delivery of therapeutics intracellularly. The diversity of polymer chemical and physical properties enables a wide range of cellular targeting and applications. We have initiated a project investigating the use of 3D ToF-SIMS imaging to localize and characterize polymer nanoparticles within cells. Though other imaging modalities can localize polymer nanoparticles in cells, ToF-SIMS presents the advantage of localization combined with chemical characterization of the particles and the surrounding cell. However, the ability to locate polymer nanoparticles in cells is complicated by the fact that most polymers are made of organic elements such as C, N, and O and produce secondary ion fragments that are the same as those generated from the surrounding cell. Herein we will demonstrate a method we have developed to isolate polymer nanoparticle signal from cell signal and generate 3D images of nanoparticle clusters within cells. Initial results with polymer nanoparticles targeted for endosomal uptake showed punctate localization of nanoparticle clusters within areas consistent with endosomal localization. Areas enriched in nanoparticles could be localized in spite of peak overlap of polymer and cellular signals.

11:00am **BI+AS-MoM9 XPS and ToF-SIMS Analysis of Functiionalized Nanoparticles: Effects of Sample Cleaning and Preparations**, *R. La Spina, V. Spampinato, I. Ojea, F.J. Rossi, D. Gilliland,* ***Giacomo Ceccone***, European Commission, Joint Research Centre, IHCP, Italy

It is recognized that detailed physico-chemical characterization of nanomaterials is becoming increasingly important both from the technological and from health and safety point of view. Moreover, an incomplete characterisation may inhibit or delay the scientific and technological impact of nanoscience and nanotechnology. However, nanomaterials characterization based on individual instrumental methods is a very challenging issue because their stability, coating and environmental effects may lead to outputs that are not very easy to interpret unequivocally. For this reason multiple analysis methods are needed to understand the nature of nanomaterials, especially if we consider that surface and interfaces are critical to the behaviours of nano-sized materials [1].

Surface chemical analysis methods, such as X-ray Photoelectron Spectroscopy (XPS) and Time of Flight Secondary Ion Mass Spectrometry, can provide an important contribution to more fully characterizing nanomaterials, so these methods should be more generally applied as part of a characterisation set of tools for nanomaterials and nanoparticles synthetized for different applications [2].

In this work, we have investigated the surface chemistry of nanoparticles, gold (AuNPS) and silica (SiO2NPs), functionalized with different thiols. In particular, the effects of sample cleaning by centrifugation and dialysis have been studied. Moreover, the challenges and problems related to sample preparation for the surface analysis will be also addressed and discussed The different steps of sample cleaning have been characterised by DLS, CPS and SEM, whilst the surface chemistry has been mainly assessed by XPS. Our results indicate that the cleaning process may influence the functionalization process. For instance, the AuNPs functionalized with CF3 terminated SAMs shows differences in the efficiency depending upon sample cleaning.

Finally, preliminary results about the behaviour of AuNPs-CF3 in protein solution (HSA) will be also presented.

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11:20am **BI+AS-MoM10 Engineered Surfaces for Bio-Relevant Applications**, ***Marlon Walker***, NIST, *A. Vaish*, University of Delaware, *D. Vanderah*, NIST/Institute for Bioscience and Biotechnology Research

Polydopamine (PDA) is a useful bio-inspired coating for surface modification. Substrates from noble metals such as gold to semiconductors such as silicon can be modified to exhibit useful biomimetic properties that may not be available on the underlying surface. However, conditions of preparation can lead to wide variability in the attributes (such as roughness) of the generated surface, and can affect subsequent functionalization and applicability. Wider adoption of the routine use of PDA is hindered by this uncertainty of the nature of the prepared surface. We present strategies for greater control of the properties of a PDA coating, which could lead to enhanced predictability of surface attributes and greater utility in surface engineering strategies.

11:40am **BI+AS-MoM11 Breast Cancer Tumor Metabolism Investigated with ToF-SIMS**, ***Lara Gamble***, *B.M. Bluestein, D.J. Graham*, University of Washington

Imaging time-of-flight secondary ion mass spectrometry (ToF-SIMS) was utilized to analyze 21 breast tissue biopsy samples. Eighteen of the biopsy samples were obtained at diagnosis and three after neoadjuvant therapy. Principal component analysis (PCA) was used to reduce the spectral data and determine major variants in the data. PCA analysis of the mass spectral data was used to test for correlation to phenotypes (ER+/PR+, HER2+, and ER-/PR-/HER2-) as well as determine the chemical changes pre and post neoadjuvant therapy.

PCA imaging analysis of the ToF-SIMS tumor tissue images showed that the combination of PCA and ToF-SIMS imaging was able to distinguish different tissue regions that correspond with similar regions in H&E stained serial tissue slices from the same block. Most notably the stromal and cellular regions could be distinguished by imaging PCA. Utilizing regions of interest (ROIs), chemical makeup of stromal regions from different tumor biopsy samples was compared.

While the cellular region showed the clearest separation for pre and post treatment chemistry, spectral PCA analysis of the stromal region shows better separation in scores plots when comparing different tumor types. Chemical analysis of the stromal regions also separated out chemical differences in triple negative tumor samples (with five different triple negative rated tumors investigated to date). In an initial sample set, the pCR (patient complete recovery) and 'near' pCR samples both score negatively in the PC2 scores plot. The key fatty acids associated with pCR samples are myristic acid (14:0), palmitic acid (16:0), stearic acid (18:0) and a 20:3 fatty acid as well as fragments of sphingomyelin and various triglycerides. The main peaks associated with the non-pCR samples were fatty acid 18:1 (consistent with oleic acid) along with cholesterol and vitamin E related peaks. Coincidentally these peaks correlate well with the loadings from the pre neoadjuvant therapy treatment samples, while the highest loadings from the pCR samples correlate with the post treatment tissue loadings.

Electronic Materials and Processing
Room: 211A - Session EM+AS+SS-MoM

Rectenna Solar Cells, MIM Diodes, and Oxide Interfaces
Moderator: John Conley, Oregon State University, Dale Kotter, RedWave Energy, Inc.

8:20am **EM+AS+SS-MoM1 Harvesting Energy with Optical Rectennas: Challenges and Innovations**, ***Garret Moddel***, University of Colorado and RedWave Energy, Inc., *S. Joshi, B. Pelz, A. Belkadi, S. Yuan*, University of Colorado at Boulder, *P. Brady, D. Kotter*, RedWave Energy, Inc. **INVITED**

Optical rectennas are of interest for radiant heat and light energy harvesting, and ultra-fast detectors that work for terahertz waves up through visible-light wavelengths. The devices work under constraints that are different from those of either microwave rectennas or conventional solar cells. These antenna-coupled diodes incorporate micron-scale antennas and diodes that must operate at frequencies in the tens to hundreds of terahertz, but the antenna size and diode speed are not the most daunting challenges. The current produced by the antenna – particularly for rectennas operating at close to visible-light frequencies – samples the diode at discrete voltages described by a quantum approach instead of at continuously varying voltages described by classical electromagnetic theory – which makes for a fascinating theory of operation. The consequence is a quantum limit to the power conversion efficiency, similar to the Shockley-Queisser limit for conventional solar cells. The optical frequency and intensity determine whether the rectenna operation can be described classically or must involve a quantum analysis. Because rectennas gather current from the entire antenna, if the light is not spatially coherent cancellation occurs, resulting in reduced efficiency. This limits the amount of power received by each diode, which further limits the diode rectification efficiency. Over the last decade the number of groups investigating various parts of rectenna technology has grown from almost none to at least 50. This growing community of researchers, with innovative solutions, is needed to meet optical rectenna challenges and enable a practical technology. Some emerging solutions will be presented.

9:00am **EM+AS+SS-MoM3 Demonstration of Traveling-Wave Metal-Insulator-Metal Diodes for 28 THz (10.6 µ m) Rectennas**, ***Bradley Pelz***, University of Colorado at Boulder, *G. Moddel*, University of Colorado at Boulder and Redwave Energy

Lumped element rectennas encounter an efficiency limitation above several terahertz due to the RC time constant of an MIM diode. A traveling-wave diode (TWD) takes advantage of nanoscale geometries to achieve a lower capacitance than that of a lumped element diode. The TWD behaves as a MIM transmission line for surface plasmons in which the rectification occurs as the wave travels down its length. Due to the distributed nature of the rectifier, the impedance seen by the antenna is the characteristic impedance of the transmission line. COMSOL simulations have shown this gives a reactive component of diode impedance that is substantially smaller than either the real component of the characteristic impedance for the TWD or the reactance from the parallel plate capacitance of an equivalently sized lumped element MIM diode. This allows for a much higher coupling efficiency from the antenna than in the case of a lumped element diode, and a substantially reduced RC time constant.

To obtain a resistance that matches that of the antenna simulations show that the TWD requires a width of 100 nm or less, which is too small for conventional lithography techniques. This small critical dimension was achieved using a germanium shadow mask technique. After fabrication, the DC junction characteristics were measured using a four-point technique. The open circuit voltage of these unbiased devices was measured under 28 THz illumination using a CO_2 laser and a lock-in amplifier. The TWD coupled to a bow tie antenna showed both polarization and power dependence. Since these measurements were completed at zero bias, the response could not have been bolometric, and the device must have been operating in energy harvesting mode.

9:20am **EM+AS+SS-MoM4 Basic Efficiency Limits for Rectenna Solar Power Conversion**, ***Heylal Mashaal***, *J.M. Gordon*, Ben-Gurion University of the Negev, Israel

The prospect of employing aperture rectennas for solar power conversion will be explored in this presentation. Sunlight is commonly viewed as incoherent – hence seemingly unsuitable for antenna harvesting – but all electromagnetic radiation exhibits spatial coherence on a sufficiently small scale. The first direct measurement of the spatial coherence of sunlight will be presented, and the ramifications for using optical concentrators that can effectively replace orders of magnitude of antenna and rectifier elements will be discussed.

Rooted in the partial spatial coherence of sunlight, a derivation of the thermodynamic limit for coherence-limited solar power conversion will be presented – an expansion of Landsberg's elegant basic bound, originally limited to incoherent converters at maximum flux concentration. The results do not depend on a particular conversion strategy. As such, they pertain to systems that span geometric to physical optics.

Last, a basic upper bound will be presented for the ability to rectify the broadband signals using a full wave rectification scheme.

Our findings indicate promising potential for rectenna power conversion.

9:40am **EM+AS+SS-MoM5 Coherence Effects in Periodic Arrays of Nano-Antennas used for Energy Harvesting and Self-Imaging**, ***Peter Lerner***, SciTech Associates, LLC, *P.H. Culter, N.M. Miskovsky*, Penn State University

Coherence effects in periodic arrays of nano-antennas used for energy harvesting and self-imaging

P. B. Lerner [1] , N. M. Miskovsky[1,2] , P. H. Cutler[1,2]

Modern technology allows the fabrication of antennas with a characteristic size comparable to the electromagnetic wavelength in the optical region. [1] This has led to the development of new technologies using nanoscale rectifying antennas (rectennas) for solar energy conversion and sensing of terahertz, IR and visible radiation. For example, a rectenna array can collect incident radiation from an emitting source and the resulting conversion efficiency and operating characteristics of the device will depend on the spatial and temporal coherence properties of the absorbed radiation. For solar radiation, the intercepted radiation by a micro- or nano-scale array of devices has a relatively narrow spatial and angular distribution. Using the Van Cittert-Zernicke Theorem, we show that the coherence length (or radius) of solar radiation on an antenna array is, or can be, tens of times larger than the characteristic wavelength of the solar spectrum, i.e., the thermal wavelength, $\lambda_T=2\pi\hbar c/(k_BT)$, which for T=5000K is about 2 microns. Such an effect is advantageous, making possible the rectification of solar radiation with nanoscale rectenna arrays, whose size is commensurate with the coherence length. Furthermore, using the van Cittert-Zernicke Theorem, we also examine the blackbody radiation emitted from an array of antennas at temperature T, which can be quasi-coherent and lead to a modified self-image, analogous to the Talbot-Lau self-imaging process [2] but with thermal rather than monochromatic radiation. This coherence of the antennas' blackbody radiation can also introduce an angular spectrum, which may be concentrated (enhanced) along certain spatial directions, giving rise to additional features not present in the original array. The self-emitted thermal radiation may be important as a non-destructive means for quality control of the array.

[1] Miskovsky, N. M., P. H. Cutler, A. Mayer, B. L. Weiss, B. Willis, T. E. Sullivan, and P. B. Lerner (2012) Nanoscale Devices for Rectification of High Frequency Radiation from the Infrared through the Visible: A New Approach, *Journal of Nanotechnology*, Article ID 512379, 19 pages, http://dx.doi.org/10.1155/2012/512379 .

[2] Gori, F. (1979) Lau Effect and Coherence Theory, *Optics Communications*, 31(1), 4.

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2 Physics Department (emeritus), Penn State University, University Park, 16802.

10:00am **EM+AS+SS-MoM6 Metamaterial Enhanced Rectenna for Efficient Energy Harvesting**, *D. Lu*, ***Won Park***, University of Colorado Boulder, *P. Brady*, Redwave Energy Inc.

Rectenna solar cell offers an important alternative to the conventional semiconductor solar cell technology. Direct rectification of electromagnetic radiation faces many challenges one of which is the high frequency of operation. Thermal emission from hot bodies peaks at 10 ~ 100 THz while solar radiation has its maximum at around 600 THz. One may circumvent this difficulty if sufficiently strong thermal radiation is available at lower frequencies. In general, thermal emission is described well by the theory of blackbody radiation while the property of the non-black surface is characterized by its emissivity. When the surface supports surface waves, however, the properties of thermal emission can deviate substantially from the blackbody radiation, offering a new avenue for engineering thermal emission. For example, spatially coherent and spectrally selective thermal emission may be achieved. The presence of surface waves also means enhanced local density of states near the surface, which consequently leads to strongly modified thermal emission intensity and spectrum in the near field. In this paper, we report a metamaterial design to achieve enhanced thermal emission at 1 THz.

Two types of metamaterial designs were investigated: a 1D array of parallel trenches and a 2D array of holes etched on copper. The metamaterial surface was designed to support surface waves resembling the surface plasmon on metal surface. Numerical simulations by the finite element method confirmed the presence of surface waves and strong electric field near the surface at 1 THz. The strongly enhanced electric field is the direct consequence of enhanced local density of states. To further confirm the surface modes can be excited by thermal emission, we also conducted finite-difference time-domain simulations in which thermal emission was calculated by using the fluctuation dissipation theorem. Once the enhanced thermal emission is confirmed, a bowtie antenna was placed close to the metamaterial surface to capture the enhanced thermal emission in the near field. The antenna was optimized to maximize the electromagnetic energy delivered to the antenna gap. Since the antenna should couple efficiently with the surface modes, the optimal antenna design became quite different from the free space bowtie antenna operating at the same frequency. The optimized metamaterial and antenna design resulted in an antenna voltage of 10 mV at 1 THz, three orders of magnitude larger than the free space antenna. Such a large enhancement makes the metamaterial approach a highly promising route to efficient energy harvesting with rectenna.

11:00am **EM+AS+SS-MoM9 Modeling of and Power from Nb-NbOx-based Nanorectenna Arrays**, ***Richard M. Osgood***, US Army NSRDEC, *J. Xu, G.E. Fernandes,* Brown University, *M. Rothschild, K. Diest,* MIT Lincoln Laboratory, *M. Kang, K.B. Kim,* Seoul National University, Republic of Korea, *L. Parameswaran*, MIT Lincoln Laboratory, *P. Periasamy,* IBM, *M. Chin,* Army Research Laboratory, *S. Kooi,* MIT Institute for Soldier Nanotechnologies, *S. Giardini,* US Army NSRDEC, *R. O'Hayre, P. Joghee*, Colorado School of Mines

We investigate arrays of "microrectennas" (with sub-micron features tuned for the near-and short-wave infrared) consisting of "stripe-teeth" metamaterial antennasconducting vertically through the coupled, underlying metal-insulator-metal (MIM) diode into a metallic substrate. Stripes, with cross-stripe resonances, conduct current out of the array, while antenna-like teeth break left-right symmetry and concentrate a high vertical electric field (E_z) at the end of the teeth at their antenna resonance. If plasmonic field enhancement and concentration reduce the capacitance and/or increase the effective voltage across the MIM diode, new research and development of large-area ultrafast optical rectennas will be enabled, requiring patterning and alignment of only the top metal layer.

Stripe-teeth arrays were designed, fabricated, and analyzed both experimentally and theoretically. Substrates were layers ("ground planes") of Nb and Al, and a Au nanowire array patterned using novel high-throughput e-beam technology.[1] Substrates were oxidized/anodized, or had oxides deposited, to form microantenna-coupled MIM diodes consisting of Al-Al_2O_3-Al, Au/Ti-NbO_x-Nb, Al-Al_2O_3-Au, Ag/Ti-NbO_x-Nb, Ag/Ti-NiO-Ni, Pt-NbO_x-Nb, after deposition of top metal layers of Ag/Ti, Au/Ti, Pt, and Al (only a few nm of Ti). Conduction through 10-25 nm thick oxide layers in the MIM diodes occurred via quantum mechanical tunneling and thermionic emission, with asymmetric barrier heights all less than 1 V except for the Al-Al_2O_3-Al diodes. The Au-Al_2O_3-Al system required modeling the "hot spot" from top metal protrusions into the Al_2O_3barrier layers and in close (tunneling) proximity to the ground plane, probably because of the surface roughness and variation in Al_2O_3 thickness; the planar-planar MIM diode model was inapplicable in this case.

The top metal was patterned into the stripe-teeth arrays. Reflective Al substrates provided sharp optical antenna resonances while Nb layers produced broader, weaker antenna resonances due to Nb absorption, similar to stripe-only arrays reported in Ref. 2. We also report the result of visible light (514 nm – 630 nm) laser illumination of Nb/NbO_x/Ag(Ti) stripe-teeth arrays, including the observation of a short-circuit current and open-circuit voltage, in response to power densities in the range 80 W/cm^2.

1. H. S. Lee, *et. al.*, "Electron beam projection nanopatterning using crystal lattice images obtained from high resolution transmission electron microscopy", Adv. Mats. **19** 4189 (2007).

2. Wu, C., *et.al.*" Large-area wide-angle spectrally selective plasmonic absorber," *Phys. Rev. B*, Vol. 84, 075102-7, 2011.

11:20am **EM+AS+SS-MoM10 Metal-Insulator-Insulator-Metal Diodes for Rectenna Applications**, ***Shijia Lin***, *N. Murari, J.F. Conley, Jr.*, Oregon State University

A metal-insulator-metal (MIM) tunnel diode has a capacitor-like structure with a thin insulating layer sandwiched by two metals. Because of their potential for femtosecond-fast transport when dominated by tunnel transport, MIMs are of interest for rectenna based solar cells, hot electron transistors, and IR detectors. The common strategy to achieving rectification in MIM devices relies on the use of dissimilar work function metal electrodes to produce an asymmetric electron tunneling barrier with polarity dependent tunneling probability. The performance of single layer MIM devices is limited by the workfuction difference that can be achieved between the electrodes and the metal-insulator band offsets. Small electron affinity oxides are limited by high V_{ON}. Large electron affinity dielectrics have small V_{ON}, but tend to have limited asymmetry due to thermal emission dominated conduction. An alternative approach to controlling asymmetry is to use nanolaminate pairs of insulators with different bandgaps and band offsets to produce asymmetric tunnel barrier metal-insulator-insulator-metal (MIIM) diodes. Asymmetry in MIIM devices may be enhanced by step tunneling[1] or defect enhanced direct tunneling.[2]

In this work, we investigate asymmetry in HfO_2/ Nb_2O_5 bilayer insulator MIIM diodes. HfO_2 and Nb_2O_5 were deposited via atomic layer deposition (ALD) using tetrakis (ethylmethylamino) hafnium (TDMAHf) and niobium ethoxide metal precursors, respectively with H_2O as the oxidant. Nanolaminate films were deposited at a chamber temperature of 250°C in one continuous run without breaking vacuum. Sputtered TaN or amorphous metals were used as the bottom electrode and evaporated Al dots were used as a top electrode. MIIM I-V asymmetry and non-linearity are shown to be a function of stack thickness, relative layer thickness, and insulator layer position with respect to the electrodes. Overall, bilayer insulators are shown to be an effective method of enhancing the performance of MIIM tunnel diodes.

1. N. Alimardani and J.F. Conley Jr, Appl. Phys. Lett. 102, 143501 (2013).

2. N. Alimardani and J.F. Conley, Jr., Appl. Phys. Lett. 105, 082902 (2014).

11:40am **EM+AS+SS-MoM11 Built-in Potential in Fe_2O_3-Cr_2O_3 Superlattices for Improved Photoexcited Carrier Separation**, ***Tiffany Kaspar***, *D.K. Schreiber, S.R. Spurgeon, S.A. Chambers*, Pacific Northwest National Laboratory

Hematite, α-Fe_2O_3, is an ideal photocatalyst to split water as a source of H_2 fuel because it is non-toxic, Earth-abundant, stable in aqueous environments, and possesses a bandgap in the visible wavelength range (~2.1 eV). However, fast photogenerated electron-hole recombination, facilitated in part by slow carrier transport kinetics, has long been identified as a major obstacle in the utilization of hematite photocatalysts. A direct method to reduce photogenerated carrier recombination is to employ heterojunctions to spatially separate excited electrons and holes. Our approach is to engineer built-in electric fields by exploiting the band alignment characteristics of epitaxial Fe_2O_3/Cr_2O_3 heterojunctions. The Fe_2O_3-Cr_2O_3 system exhibits non-commutative band offsets which differ by approximately 0.4 eV depending on the order of deposition. The non-commutative band offset properties of Fe_2O_3-Cr_2O_3 interfaces can be utilized in a superlattice structure, deposited by oxide molecular beam epitaxy, to build up an intrinsic electric field; this potential may be sufficient to spatially separate photogenerated electrons and holes. We demonstrate precise control over the Fe_2O_3-Cr_2O_3 interface structure with atomic-resolution atom probe tomography and scanning transmission electron microscopy. Direct evidence that Fe_2O_3-Cr_2O_3 superlattice layers generate an intrinsic built-in potential is observed with x-ray photoelectron spectroscopy. The individual interfacial band offset values, and thus the overall potential, can be tailored by altering the cation stoichiometry at the interfaces. Doping the component layers to improve transport characteristics requires a deep understanding of the dopant-induced electronic structure changes. To illustrate how the built-in potential in optimized Fe_2O_3-Cr_2O_3 superlattice structures can be harnessed to drive holes to the surface and electrons into the bulk, photoconductivity and photochemical degradation results will be presented.

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 1.0~2.0 x 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 Ga2O3 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.

References

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[2] V. Chobpattana et al., J. Appl. Phys. 114 (2013), 154108

[3] H. Chen et al., IEEE TED 59 (2012), 2383-2389

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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.

1. Eichfeld, S. M.; Hossain, L.; Lin, Y.-C.; Piasecki, A. F.; Kupp, B.; Birdwell, A. G. G.; Burke, R. A.; Lu, N.; Peng, X.; Li, J.; et al. Highly Scalable, Atomically Thin WSe2 Grown via Metal-Organic Chemical Vapor Deposition. ACS Nano 2015.

2. Y.C. Lin, C.-Y. Chang, R. Ghosh,J.Li, H.Zhu, R.Addou, B.Diaconescu, T.Ohta, X.Peng, N.Lu, M.J. Kim, J.T. Robinson, R.M.Wallace, T.Mayer, S.Datta, L.J. Li, J.A. Robinson; Atomically Thin Heterostructures based on Single-Layer Tungsten Diselenide and Graphene; *Nano Letters*

3. M. S. Bresnehan, G. Bhimanapati, K. Wang, D.Snyder, J.A.Robinson; Impact of Copper Overpressure on the Synthesis of Hexagonal Boron

Nitride Atomic Layers; *ACS Appl. Mater. Interfaces*, 6, 16755–16762 (2014)

4. S.M. Eichfeld, C.M. Eichfeld, Y.C. Lin, L. Hossain, J.A. Robinson; Rapid, non-destructive evaluation of ultrathin WSe2 using spectroscopic ellipsometry; *APL Materials* 2 (9), 092508

5. Y.C. Lin, N. Lu, N. Perea-Lopez, J. Li, C.H. Lee, Z.Lin, P.N. Browning, M.S. Bresnehan, L. Calderin, M.J. Kim, T.S. Mayer, M. Terrones, J.A. Robinson; Direct Synthesis of van der Waals Solids on Epitaxial Graphene; *ACS Nano* 8 (4), 3715-3723 (2014)

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 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.

[1] "Chemical potential and quantum Hall ferromagnetism in bilayer graphene", K. Lee, B. Fallahazad, J. Xue, D. C. Dillen, K. Kim, T. Taniguchi, K. Watanabe, E. Tutuc, Science 345, 58 (2014).

[2] "Gate-Tunable Resonant Tunneling in Double Bilayer Graphene Heterostructures", B. Fallahazad, K. Lee, S. Kang, J. Xue, S. Larentis, C. Corbet, K. Kim, H. C. P. Movva, T. Taniguchi, K. Watanabe, L. F. Register, S. K. Banerjee, E. Tutuc, Nano Letters 15, 428 (2015).

[3] "Bilayer Graphene-Hexagonal Boron Nitride Heterostructure Negative Differential Resistance Interlayer Tunnel FET", S. Kang, B. Fallahazad, K. Lee, H. C. P. Movva, K. Kim, C. Corbet, T. Taniguchi, K. Watanabe, L. Colombo, L. F. Register, E. Tutuc, S. K. Banerjee, IEEE Electron Device Letters 36, 405 (2015)

[4] "Band Offset and Negative Compressibility in Graphene-MoS_2 Heterostructures", S. Larentis, J. R. Tolsma, B. Fallahazad, D. C. Dillen, K. Kim, A. H. MacDonald, E. Tutuc, Nano Letters 14, 2039 (2014).

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

IPF on Mesoscale Science and Technology of Materials and Metamaterials
Room: 210F - Session IPF+MS-MoM

Materials for Energy Generation and Storage (8:20-10:20) & Mesoscale Phenomena in the Biosciences I (10:40-12:00)
Moderator: Alain Diebold, SUNY College of Nanoscale Science and Engineering, Carolyn Larabell, University of California, San Francisco

8:20am **IPF+MS-MoM1 Synthesis and Behavior of Nanostructures in Mesoscale Architectures**, ***SangBok Lee***, *G.W. Rubloff, E. Gillette, C. Liu,* University of Maryland, College Park, *X. Chen,* Lam Research Corporation, *J. Hu, S. Wittenberg, L. Graham,* University of Maryland, College Park, *P. Banerjee*, Washington University, St. Louis **INVITED**

As advanced nanostructured electrodes continue to push boundaries for both high power and high energy, it will become increasingly important to understand how structure on the mesoscale impacts charge transport and electrochemical reactions. Understanding the influence of structure on ionic and electronic transport behavior, as well as its influence on degradation is highly essential to design and control improved electrodes. Here, we describe the fabrication of two types of electrodes; one with electrodes constructed in the most simple cylindrical nanopores - "all-in-one nanopore battery" - and the other with electrodes in controllable 3D interconnecting pore network to propose a strategy for bridging the gap between precision, self-aligned nanostructure electrodes and disordered, high density electrodes. These architectures highlight some of the challenges of characterizing tortuosity and porosity in nanostructures, but also provides an opportunity to work with a systematically variable mesoscale electrode structure.

9:00am **IPF+MS-MoM3 Ultralight Microlattices: Defining the Limits of Lightweight Materials**, ***William Carter***, HRL Laboratories, LLC **INVITED**

Design of "materials architecture" is emerging as a new and complimentary approach to classical materials selection in engineering design. By adjusting the geometric arrangement of solid phases and voids within a material, it is possible to extend the achievable property space for lightweight materials and functional coatings. Optimal microlattice materials that can be formed in a wide range of architectures and base materials, with properties spanning from unprecedented low density and surprisingly high mechanical recovery to structural alternatives to honeycomb and foams. The starting polymer microlattice templates are created using an array of interpenetrating self-forming photopolymer waveguides from a single exposure mask. Free-standing hollow micro-lattice materials can be formed based on a wide range of high performance thin films (metals, ceramics and polymers) by coating a micro-lattice template followed by subsequent removal of the template. The process enables precise and independent control over micro-lattice architecture at all levels of structural hierarchy (~100nm up to ~10cm). This technique is also inherently scalable to low-cost high-throughput manufacturing (~10-60 second exposure), highly scalable to large sizes (m2), enabling practical design and fabrication of a wide range of lattice materials including metals, polymers and ceramics.

9:40am **IPF+MS-MoM5 "Can Opto-Electronics Provide the Motive Power for Future Vehicles?"**, ***Eli Yablonovitch***, University of California, Berkeley **INVITED**

A new scientific principle[1] has produced record-breaking solar cells. The 28.8% single-junction solar efficiency record, by Alta Devices [2], was achieved by recognizing the importance of extracting luminescent emission. This is exemplified by the mantra: "A great solar cell also needs to be a great LED". It was essential to remove the original semiconductor substrate, which absorbed luminescence, and to replace it with a high reflectivity mirror. The solar efficiency record crept up as the rear reflectivity behind the photovoltaic film was increased, 96% reflectivity -- 97% -- 98% luminescent reflectivity;-- each produced a new world efficiency record.

In thermo-photovoltaics, high energy photons from a thermal source are converted to electricity. The question is what to do about the majority of low energy infrared photons? It was recognized that the semiconductor band-edge itself can provide excellent spectral filtering for thermophotovoltaics, efficiently reflecting the unused infrared radiation back to the heat source. Exactly those low energy photons that fail to produce an electron-hole pair, are the photons that need to be recycled.

Thus the effort to reflect band-edge luminescence in solar cells has serendipitously created the technology to reflect all infrared wavelengths, which can revolutionize thermo-photovoltaics. We have never before had such high rear reflectivity for sub-bandgap radiation, permitting step-function spectral control of the unused infrared photons for the first time. This enables conversion from heat[3] to electricity with >50% efficiency. Such a lightweight "engine" can provide power to electric cars, aerial vehicles, spacecraft, homes, and stationary power plants.

1. O. D. Miller, Eli Yablonovitch, and S. R. Kurtz, "Strong Internal and External Luminescence as Solar Cells Approach the Shockley–Queisser Limit", IEEE J. Photovoltaics, vol. 2, pp. 303-311 (2012). DOI: 10.1109/JPHOTOV.2012.2198434

2. Kayes, B.M.; Hui Nie; Twist, R.; Spruytte, S.G.; Reinhardt, F.; Kizilyalli, I.C.; Higashi, G.S. "27.6% Conversion Efficiency, A New Record For Single-Junction Solar Cells Under 1 Sun Illumination" Proceedings of 37th IEEE Photovoltaic Specialists Conference (PVSC 2011)Pages: 4-8, DOI: 10.1109/PVSC.2011.6185831

3. The heat source can be combustion, radio-activity, or solar thermal.

10:40am **IPF+MS-MoM8 The Convergence of Synthetic Biology and Biofabrication: Guiding Biological Function at the Mesoscale**, ***William Bentley***, Fischell Department of Bioengineering, University of Maryland **INVITED**

Synthetic biology provides a means for articulating concepts into new products and products. Its toolbox is extensive, including the ability to create synthetic genomes and tailor their regulation. Early successes augmented the cell's biosynthetic capacity and rewired its regulation, transforming our ability to produce products ranging from small molecules to fully functional therapeutic proteins at high yield. Also, the theoretical formalisms of metabolic engineering provided a basis for optimally routing its biochemical flux. With pathway analysis and optimization, cells are now engineered to produce large quantities of economically important molecules. Indeed, many "green" routes to chemical synthesis have appeared and many more are emerging. There exists great enthusiasm and investment to revolutionize several industries. Importantly, these activities have focused largely on the cell's intracellular biochemical network and relied less on molecular cues from the immediate surroundings. Largely untapped within synthetic biology are the signaling motifs that guide cell processes and interactions among communicating populations. That is, signal molecules guide many cellular processes and these can be exploited to endow cells with "executive" function, where decision events are programmed and cells carry out tasks in addition to making products. That is, the cells themselves can be the primary "products" of synthetic biology – putting them to work in complex "noisy" environments will require tailoring their exposure to chemical cues. For example, we may eventually use engineered bacteria to fight cancer, cure diabetes, or "tune" the microbiome in our GI tracts. Biofabrication, the use of biological components and biological processes for assembly, can provide a means for tailoring hierarchical order in biological systems. We exploit the principles of biofabrication to create 3D "test tracks" where chemical cues can be spatiotemporally controlled and task-accomplishing bacteria can be appropriately designed. We will discuss the link between synthetic biology and biofabrication and highlight the potential for new discovery as well as process and product innovation.

11:20am **IPF+MS-MoM10 Using Mesoscale Modeling to Design Materials that Compute: Coupling Self-Oscillating Gels and Piezoelectric Films**, *V.V. Yashin, S.P. Levitan,* ***Anna C. Balazs***, University of Pittsburgh **INVITED**

Lightweight, deformable materials that can sense and respond to human touch and motion can be the basis of future wearable computers, where the material itself will be capable of performing computations. To facilitate the creation of "materials that compute", we draw from two emerging modalities for computation: chemical computing, which relies on reaction-diffusion mechanisms to perform operations, and oscillatory computing, which performs pattern recognition through synchronization of coupled oscillators. Chemical computing systems, however, suffer from the fact that the reacting species are coupled only locally; the coupling is limited by diffusion as the chemical waves propagate throughout the system. Additionally, oscillatory computing systems have not utilized a potentially wearable material. To address both these limitations, we develop the first model for coupling self-oscillating polymer gels to a piezoelectric (PZ) micro-electro-mechanical system (MEMS). The resulting transduction between chemo-mechanical and electrical energy creates signals that can be propagated quickly over long distances and thus, permits remote, non-diffusively coupled oscillators to communicate and synchronize. Moreover, the oscillators can be organized into arbitrary topologies because the electrical connections lift the limitations of diffusive coupling. Using our model, we predict the synchronization behavior that can be used for computational tasks, ultimately enabling "materials that compute."

In-Situ Spectroscopy and Microscopy Focus Topic
Room: 211C - Session IS+AS+SS-MoM

Fundamental Studies of Surface Chemistry of Single Crystal and Nanomaterials under Reaction Conditions

Moderator: Franklin (Feng) Tao, University of Kansas, Zili Wu, Oak Ridge National Laboratory

8:20am **IS+AS+SS-MoM1 Hot Electron In-Situ Surface Chemistry at Oxide-Metal Interfaces. Foundations of Acid-Base Catalysis**, ***Gabor Somorjai***, University of California, Berkeley **INVITED**

The development of Catalytic Metal-Semiconductor Nanodiodes (CMSN) to measure the flow of electrons excited during exothermic catalytic reactions at the metal interface proved that oxidation on platinum generates a steady flux of hot electrons [1] Evidence is presented that the steady state of chemicurrent is correlated to the turnover frequency and that the exothermic hot electron production during reactions on transition metal particles may be widespread. The CO/O2 and H2/O2 reactions were studied most frequently by this method and semiconductors included TiO2, GaN, CoOx, NbOx and TaOx Charge transport between the metal and oxide interfaces also influences the product distribution of multipath reactions. These were shown in the hydrogenation of furfural and croton aldehyde at platinum/TiO2 interfaces as compared to the platinum/silica interfaces [2]. The oxide-metal interfaces appear to produce ions, which carry out reactions that have long been called by the organic chemistry community as acid base catalysis. The typical catalytic structure is mesoporous oxide that is produced to hold the metal nanoparticles. The structures produce high surface area oxide metal interfaces and this is a catalytic architecture for acid base catalysis. Studies in changing the transition metal oxide using a single metal of platinum as nanoparticles, shows the tremendous amplification effect of the oxide metal interfaces in the reactions such as the carbon monoxide oxidation. Platinum alone produces on silica three orders of magnitude less CO2 by the CO oxidation process than on cobalt oxide, that is the most active of these acid base oxide metal interface catalytic systems [3]. Nevertheless, not just cobalt oxide, but nickel oxide, manganese oxide, and iron oxide, produces much higher activity for this reaction than platinum alone. In other reactions, when n-hexane isomerization or cyclisation reactions studied, the pure oxides niobium or tantalum do not produce any reaction other than cracking two smaller molecular fragments. However, at the platinum-oxide interfaces with niobium oxide or tantalum oxide, almost 100% selectivity for isomerization could be achieved [4]. Thus it appears that charge catalysis plays a very important role, which is equal in importance to the role of pure metal covalent catalysis that produces molecules without any apparent charge flow. Generation of hot electron flows and the catalytic activity of two-dimensional arrays of colloidal Pt nanoparticles with different sizes are investigated using catalytic nanodiodes. Pt nanoparticles of smaller size lead to higher chemicurrent yield, which is associated with the shorter travel length for the hot electrons, compared with their inelastic mean free path [5]. In many oxide supports microporous sites are used, which are less than 1 nm in size and do not allow the larger platinum nanoparticles inside these pores. In that case, the metal that is used to create the catalysts are deposited on the outside surface of the microporous support. This sort of system, where the metal is outside, but the acidic microporous oxides are inside, can be active only by a spill over of the reaction intermediates from the metal to the oxide - and this is quite well known. However if the micropores are substituted by mesopores in the oxide phase the metal nanoparticles can go inside and then single site oxide-metal interface catalysis commences. These two different catalytic processes, where both the oxide and the metal are catalytically active, deserve attention and distinction.

9:00am **IS+AS+SS-MoM3 In-situ GISAXS/GIXAS Characterization of $Co_{1-x}Pt_x$ Bimetallic Clusters under H_2 and CO + H_2 Mixture**, ***Bing Yang***, Material Science Division, Argonne National Laboratory*, G. Khadra, J. Tuaillon-Combes,* Institut Lumière Matière, University Lyon & CNRS, France*, E. Tyo,* Material Science Division, Argonne National Laboratory*, S. Seifert,* X-ray Science Division, Argonne National Laboratory*, X. Chen,* Department of Mechanical Engineering, Northwestern University*, V. Dupuis,* Institut Lumière Matière, University Lyon & CNRS, France*, S. Vajda*, Material Science Division, Argonne National Laboratory

CoPt alloy particles have recently attracted great interests for their excellent catalytic and magneticproperties. The alloy phase of cobalt and platinum may create dual-functional sites at the mixed interface which enables novel catalytic properties and synergic effect at nanometer scale. In-situ characterization is thus essential to probe the structure and composition of bimetallic clusters under reaction conditions in a catalytic process of interest.

$Co_{1-x}Pt_x$ bimetallic clusters with atomic-precise Pt/Co atomic ratio (x=0, 0.25, 0.5, 0.75, 1) were synthesized using mass-selected low energy clusters beam deposition (LECBD) technique and soft-landed onto the amorphous alumina thin film prepared by atomic layer deposition (ALD). The median diameter of size-selected $Co_{1-x}Pt_x$ alloy clusters is 3nm with size dispersion lower than 10 % according to transmission electron microscopy (TEM). Utilizing X-ray photoemission spectroscopy (XPS), the oxidation state of as-made clusters as well as the aged particles after extended exposure to air was characterized. After exposure to air, both cobalt and platinum species in the bimetallic clusters are found to be oxidized, while the shift of their covalent state exhibits a non-linear correlation with their atomic composition (Pt/Co).

Utilizing *in-situ* grazing incidence small-angle X-ray scattering and X-ray absorption spectroscopy (GISAXS/GIXAS), the evolution of particle size/shape and the oxidation state of the individual metals are monitored under atmosphere reaction conditions. The as-made $Co_{1-x}Pt_x$ clusters were first pretreated with hydrogen and further exposed to CO and H_2 mixture up to 225°C. The change in the oxidation state of Co and Pt of the supported bimetallic clusters exhibited a non-linear dependency on the Pt/Co atomic ratio. For example, low Pt/Co ratio (x≤0.5) facilitates the formation of $Co(OH)_2$, whereas, high Pt/Co ratio (x=0.75) stabilizes Co_3O_4 composition instead, due to the formation of Co@Pt core-shell structure where the platinum shell inhibits the reduction of cobalt in the core of the $Co_{1-x}Pt_x$ alloy clusters.

In this work, we have demonstrated *in-situ* measurement of particle size/shape and the oxidation state of supported $Co_{1-x}Pt_x$ bimetallic clusters under operating conditions, and elucidated the different surface structure and chemical state with respect to their atomic ratio. The obtained results indicate ways for optimizing the composition of binary alloy clusters for catalysis.

9:20am **IS+AS+SS-MoM4 Novel Surface Oxide on Pt(111) as the Active Phase for NO and CO Oxidation Studied with the ReactorSTM**, ***Matthijs van Spronsen****, *J.W.M. Frenken, I.M.N. Groot*, Leiden University, Netherlands

Platinum finds its main application as a car catalyst to control the emission of exhaust gases. Although automotive catalysis has been extensively investigated, challenges still exist. One of the challenges arises when increasing the oxygen/fuel ratio. Under oxygen-rich reaction conditions, much uncertainty exist about the structure of the active surface phase. This is even true for the Pt(111) surface, which is the facet lowest in energy and the simplest model catalysts available.

An early *operando* Scanning Tunneling Microscopy (STM) study [1] showed a stepwise increase in CO oxidation activity at oxygen-rich conditions. This increase concurred with a dramatic and instantaneous morphology change. From the STM images, the atomic structure could not be resolved, but roughening on a long length scale was observed. Under

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*** Morton S. Traum Award Finalist**

similar conditions, Surface X-ray Diffraction found the formation of thin, bulk-like α-PtO_2 [2]. Surprisingly, a theoretical study concluded that this oxide is inert to CO oxidation [3].

With the high-pressure, high-temperature ReactorSTM [4], we studied the oxidation of Pt(111) both by exposing to O_2 and to NO oxidation conditions.

Upon oxidation with O_2 (1.0 bar, 423-523 K), we found a stable surface oxide consisting of triangles assembled in a 'spoked-wheel' superstructure. In addition, we found a second structure consisting of a lifted-row pattern. The two structures were coexisting on different regions on the surface. The lifted-row structure was becoming more predominant at higher O_2 pressure. We propose that both oxides share the same building block, which are expanded Pt oxide rows.

After evacuation of the reactor, the ordered structures disappeared, although some remnants remained. The surface oxidation is a clear example of the pressure-gap effect. Furthermore, lower-temperature (291-323 K) experiments did not yield any ordered structure showing the dependence on atomic mobility.

Exposure of Pt(111) to NO and O_2 or exposure to NO_2 resulted in the formation of a mixture of small domains of both the spoked-wheel and the lifted-row structures.

The surface oxidation was accompanied with roughening of terraces. This is attributed to relaxation of adsorbate-induced stress on the surface. Identical roughness development was previously found under CO oxidation conditions [1]. Therefore, we argue that a surface oxide was also the relevant structure under CO oxidation conditions.

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9:40am **IS+AS+SS-MoM5** ***In Operando* Study of Dimethyl Methylphosphonate Degradation Over Metallic and Oxidized Cu(111) Surfaces via Ambient-Pressure X-ray Photoelectron Spectroscopy**

Lena Trotochaud*, A.R. Head,* Lawrence Berkeley National Laboratory (LBNL)*, Y. Yu,* University of Maryland*, O. Karslioglu, M. Hartl,* LBNL*, B. Eichhorn,* University of Maryland*, H. Bluhm*, LBNL

Filtration systems for absorption and decomposition of chemical warfare agents (CWAs) are the first line of defense against exposure to these toxic compounds. Composite materials (such as ASZM-TEDA) commonly used in filtration systems consist of high-surface-area carbon supports impregnated with various metals and metal oxides. Despite decades of work to develop highly effective and versatile filtration materials with long-term usability, little is known about the mechanisms of CWA degradation by material surfaces and catalyst deactivation and poisoning, in part due to the challenges involved with spectroscopic characterization of catalyst surfaces under operating conditions. Enabling the rational design of more advanced filtration and decomposition materials for broad-spectrum protection against CWAs and other toxic industrial compounds requires a sophisticated understanding of the chemical mechanisms behind CWA sorption and degradation on the molecular scale.

We will present the surface spectroscopic study of metallic and oxidized Cu(111) single crystal surfaces for catalytic decomposition of dimethyl methylphosphonate (DMMP), a CWA simulant. Ambient-pressure X-ray photoelectron spectroscopy (APXPS) enables examination of these surfaces during DMMP adsorption and decomposition. Initial experiments indicate that adsorption of DMMP on Cu(111) is observed at pressures as low as 1×10^{-7} Torr, and degradation of DMMP is observed at this pressure and higher (60 mTorr) at room temperature. Possible mechanisms of DMMP degradation and deactivation of the surface will also be discussed.

10:00am **IS+AS+SS-MoM6 Bridging the Pressure and Materials Gap between Surface Science and Catalysis: Probing the Surface of Metal Oxide Nanoparticles under Reaction Conditions**

Maria Kipreos*, M. Foster*, University of Massachusetts, Boston

Traditionally, surface science employs ultra-high vacuum, cryogenic conditions and well defined crystal planes; however, heterogeneous catalysis and photocatalysis occur in ambient conditions with complex substrates composed of several crystal planes. Consequently, materials and pressure gaps exist that need to be bridged in order to better understand the surface chemistry of catalysts under reaction conditions. Metal oxide particles employed in catalysis contain a complex matrix of crystal planes, metal/oxygen bonds, metal/hydroxyl bonds, and oxide/water interactions. We utilize *in situ* Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) to monitor reactions from ambient to high pressures between gaseous adsorbates (water, formic acid, and methanol) and metal oxide particles (TiO_2 and ZnO, semiconductors and ZrO_2,an insulator) commonly used as components of catalysts. The internal and external scattering of light that occurs in DRIFTS is well suited for analysis of reactions on the surface of metal oxide nanoparticles. Spectral shifts in frequency, peak area and width values, and absorbance values are used to interpret the structure and reactivity of the surface. Additionally, the use of Confocal Raman Spectroscopy aids in determining the structural variability in these substrates. The use of gaseous probes and these instrumental techniques provides a better understanding of the structure and reactivity of solid nanoparticles surfaces.

10:40am **IS+AS+SS-MoM8 The Use of Integrated *Operando, In Situ* and DFT Techniques to Unravel the Steps of Heterogeneous Catalytic Reactions**

Fabio Ribeiro*, W.N. Delgass, J. Greeley, R. Gounder, J. Miller,* Purdue University*, W.F. Schneider*, University of Notre Dame

INVITED

Our quest to understand catalysis is limited by our ability to observe the active site while it is turning over. To facilitate this task we developed model catalysts where the active sites are deposited on the external surface area of an appropriate support. Effective characterization, however, happens only with the simultaneous measurement of the rate of reaction while the catalyst is in operation, called operando measurements. The application of operando techniques is becoming a more common tool to help unravel catalytic functions. Our group has custom-built an operando reactor for the measurement of X-ray absorption spectroscopy. While operando measurements are a major improvement, they provide a static picture of a system that is actually dynamic. Dynamic techniques where the catalyst kinetic and structural properties can be followed simultaneously with a time resolution of a fraction of a turnover are the techniques of choice. We will show examples using a transmission FTIR cell we developed. The great advantage and sometimes necessity of performing experiments in the dynamic and operando modes will be discussed. The help from theory will also be illustrated.

11:20am **IS+AS+SS-MoM10 In Situ XPS Of Graphene-Catalyst Interactions During Chemical Vapor Deposition**

Robert Weatherup, Lawrence Berkeley National Laboratory

Critical to controlling the growth of graphene and carbon nanotubes during chemical vapor deposition (CVD) is a detailed understanding of the role of the catalyst, however this remains incomplete due the wide parameter space. Here we investigate the dynamics of graphene-catalyst interactions during CVD using time- and depth-resolved X-ray photoelectron spectroscopy[1-2], in situ scanning tunneling microscopy,[3] and grand canonical Monte Carlo simulations coupled to a tight-binding model[1]. We focus on Ni(111) as a model catalyst surface and probe in-operando a wide range of hydrocarbon exposure pressures (10^{-6}-10^{-1} mbar). The key atomistic mechanisms of graphene formation on Ni are thereby revealed and our data highlights an interdependency between the distribution of carbon close to the catalyst surface and the strength of the graphene-catalyst interaction.

The strong interaction of epitaxial graphene with Ni(111) causes a depletion of dissolved carbon close to the catalyst surface, which prevents additional layer formation leading to a self-limiting graphene growth behavior for low exposure pressures (10^{-6}-10^{-3} mbar). Increasing the hydrocarbon pressure further (to ~10^{-1} mbar) leads to weakening of the graphene-Ni(111) interaction accompanied by additional graphene layer formation, mediated by an increased concentration of near-surface dissolved carbon. We also reveal that the growth of more weakly adhered, rotated graphene on Ni(111) is linked to an initially higher level of near-surface carbon compared to the case of epitaxial graphene growth. We relate these results to the simple kinetic growth model that we have previously established,[6] and use them to consistently explain previous graphene CVD results in the literature. The key implications for graphene growth control and their relevance to carbon nanotube growth are thereby highlighted.

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11:40am **IS+AS+SS-MoM11 Mechanism Study for Salen Ligand Homogeneous Catalyst in a Heterogeneous Catalysis System**

Niclas Johansson*, S. Chaudhary, A.R. Head, O. Snezhkova, J.N. Andersen, J. Knudsen, J. Schnadt*, Lund University, Sweden

Surface-immobilization of transition metal complexes otherwise used as homogeneous catalysts, i.e. in the same (solution) phase as the reactants and products, and their use as heterogeneous catalysts has been an active field of research for many years. The attractiveness of the idea of surface-immobilization lies in the potential to significantly increase the efficiency and selectivity of heterogeneous catalysts [1], the ease of catalyst and product separation [1], and the fact that the need for solvents and highly oxidizing agents might be eliminated in the heterogeneous system.

Here we direct our attention towards the transition metal Mn(III)-salen complex[R,R(-)N,N'Bis(3,5-di-t-butylsalicylidene, 1,2-cyclohexane diaminomanganese(III)chloride) which have been shown to be very effective homogeneous catalysts for enatioselective epoxidation of unfunctionalised olefins. Yet, while much research has been done to investigate the salen complexes' catalytic properties in the homogeneous phase, very few surface science studies have been performed [2,3].

Here we report a study starting from standard UHV conditions and bridging the pressure gap into more realistic conditions. Here, we will show UHV spectra coupled to Torr-range Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS).

We investigated propylene(C_2H_6) epoxidation reaction using surface-deposited Mn(III)-Salen on Au(111) as catalyst. With APXPS we were able to follow the electronic structure changes during reaction conditions in a gas mixture of propylene and oxygen. The spectra acquired show gas phase interactions and changes was found that were specific to the gas mixture. Surprisingly, O 1s spectra acquired at room temperature shows CO_2 which indicates complete oxidation of propylene. This result was further confirmed with a mass spectrometer in direct connection with the reaction chamber. Indeed, the complexes are active even in a heterogeneous system supporting the possibility of transferring homogeneous catalysts into heterogeneous catalytical systems.

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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.

Research supported in part by the Center for Nanophase Materials Sciences, sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, US Department of Energy.

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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 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.

Plasma Science and Technology
Room: 210A - Session PS+SE-MoM

Atmospheric Pressure Plasma Processing I
Moderator: François Reniers, Université Libre de Bruxelles

9:00am **PS+SE-MoM3 Modeling Non-Equilibrium Plasma Jets at Atmospheric Pressure**, ***Leanne Pitchford***, CNRS and University of Toulouse 3, France **INVITED**

The considerable recent interest in 'microdischarges' (discharges in small, spatially-confined geometries) is largely due to their remarkable stability. That is, stable, non-thermal, atmospheric-pressure plasmas can be generated and maintained in electric discharges in small geometries. Further interest in microdischarges is due to the fact that 'plasma jets', initiated from microdischarges operating with pulsed or RF excitation and with an axial

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*** Peter Mark Memorial Award Winner**

† NSTD Recognition Award

helium flow, can propagate in the helium jet which extends some distance (cm's) into the open air past the exit of the microdischarge, while causing little or no increase in the gas temperature. Fast imaging shows that most of the light emitted by the plasma jet is produced in a small 'plasma bullet' that propagates in the helium jet at speeds of some tens of kilometers per second. The possibility to generate non-thermal plasmas in ambient air has incited considerable interest for applications in the biomedical field, among others.

Modeling is an important tool for developing an understanding of microdischarges. It has been shown that the plasma jet is very similar to a cathode streamer (ionization wave) guided by air surrounding the more easily-ionized helium jet. This talk will focus on results from two-dimensional fluid modeling. The properties of the streamer in helium and of the plasma channel behind the streamer head as a function of parameters such as the electrode geometry and voltage pulse waveform will be discussed. We will focus in particular on the the configuration developed by the team of Vincent Puech at the Laboratoire de Physique des Gaz et des Plasmas at the Université Paris Sud in Orsay. This configuration consists of a dielectric tube, some mm in diameter, with an inner, hollow electrode (high voltage) and an outer ring electrode (ground). A discharge is initiated inside the dielectric tube by applying high voltage pulse (some kV's with 100 ns risetime) to the inner electrode. Models reproduce the main features of plasma jets observed experimentally, and quantities such as energy deposition in the plasma jet itself can be obtained from modeling, whereas it is much more difficult to extract such information from experiments. More work is needed to quantify the plasma chemistry triggered by the plasma jet and in particular of the influence of the remnant excitation and ionization on the properties of the subsequent plasma jets.

9:40am **PS+SE-MoM5 Vacuum Ultraviolet Polymer Etching and Modification by a Remote Atmospheric Pressure Plasma Jet**, ***Andrew Knoll***, *P. Luan, E.A.J. Bartis, G.S. Oehrlein*, University of Maryland, College Park

In this study, we investigate the etching mechanism of atmospheric pressure plasma jet (APPJ) treated poly(methyl methacrylate)-based 193 nm photoresist polymer and polystyrene-based 248 nm photoresist polymer using *in situ* ellipsometry to monitor film thickness and refractive index in real time. The kHz-driven, two-ring electrode APPJ used in this work operated with low admixtures of O_2 and N_2 to Ar feed gas flowed at 2 slm. Additionally, we used attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and x-ray photoelectron spectroscopy to characterize the surface modifications post treatment. With pure argon feed gas, we observed etching of the photoresist polymers even when the visible plume is not in direct contact with the polymer surface. This etching rate is sensitive to the Ar gas flow rate and local gas environment. APPJ treatments were compared to a surface microdischarge source with a O_2/ N_2 gas flow added but no etching was seen for that source. Furthermore, the etching was shown to be directional by placing a grounded mesh directly over the sample during treatment. No etching was seen without direct line of sight from source to sample. Optical filters were used to investigate the effect of high energy photons on polymer etching and modification. When a MgF_2 filter with a 114 nm cutoff wavelegth is placed directly over the sample, etching still occurs. When a sapphire filter with cutoff wavelength of 142 nm is used, no etching is seen. Ar_2* excimer species are known to be created in atmospheric pressure plasma and emit photons at 128 nm. Vacuum-ultraviolet (VUV)-induced etching is further supported by experiments that show that etching increases in nitrogen environments compared to oxygen environments as oxygen more effectively absorbs VUV radiation. ATR-FTIR of treated samples shows comparable bulk modifications with or without MgF_2 filter over the sample. These results are consistent with photoresists treated with VUV from low pressure plasma. APPJs are sources of a variety of reactive chemical species which can be used for numerous industrial and medical applications. While the VUV effect of APPJ sources on biodeactivation has been investgiated[1,2], polymer etching has not been seen prior to this work. The authors gratefully acknowledge financial support by US Department of Energy (DE-SC0001939) and National Science Foundation (PHY-1415353).

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10:00am **PS+SE-MoM6 Recent Development and Application of Low Cost and Portable Atmospheric Pressure Microplasma Generation Devices**, ***Cheng-Che Hsu***, *P.K. Kao, Y.J. Yang, Y.H. Huang*, National Taiwan University, Taiwan, Republic of China

Low cost and portable atmospheric pressure microplasma generation devices (MGD) offer great opportunities in several applications when plasmas in-situ, on-demand and/or in-field are desired. This study presents the development of simple and economical MGD made on copper clad laminate. This MGD can be sustained using a portable power supply (less than two pounds) that can be powered by 12V-batteries. Matching of the device capacitance with power arrangement is extremely important for this power to properly function. The use of such devices for gas conversion, selective area treatment, and fabrication microfluidic paper-based analytical device (μPAD) on demand will be presented. Such a MGD can be used to perform surface patterning of hydrophobic/hydrophilic contrasts with sub-mm spatial resolution and to effectively decompose CO2 into CO. In addition, using this MGD to fabricate μPADs is demonstrated. With a proper design of the MGD electrode geometry, μPADs with 500 μm-wide flow channels can be fabricated within 1 min and with a cost of less than $USD 0.1/device. We then test the μPADs by performing quantitative colorimetric assays and establish calibration charts for detection of glucose and nitrite. The results show a linear response to glucose assay for 1 -50 mM and nitrite assay for 0.1 -5 mM . This low cost and portable MGD can be used for in-field diagnostic tests, and is believed to bring impact to the field of biomedical analysis, environmental monitoring, and food safety survey.

10:40am **PS+SE-MoM8 Experimental Study of Micron-Scale, Field Emission-Driven Microplasmas**, ***Mihai Bilici***, *C.R. Boyle,* Case Western Reserve University, *D.B. Go,* University of Notre Dame, *R.M. Sankaran*, Case Western Reserve University

Microplasmas are miniaturized versions of low-pressure, direct-current glow discharges that can be stabilized at high pressures, up to and exceeding atmospheric pressure. In particular, atmospheric-operation has resulted in interest in their applications in materials processing, environmental remediation, and ionization sources for mass spectrometry. At these small electrode dimensions, new properties emerge that may also be important for fundamental study. For example, as the electrode gap is reduced to less than ~10 μm, gas breakdown has been found to deviate from Paschen's law due to an additional contribution to electron emission from field emission. In addition, field emission leads to a "pre-breakdown" regime where gas-phase electrons can interact with the background gas and even ionize the gas before complete breakdown occurs. However, to date there is little experimental evidence of these field-emission driven microplasmas to support theoretical predictions.

Here, we present a study of field-emission driven microplasmas using a custom-built tip-to-plane microplasma setup with environmental control and nanometer-resolution stepper motor control. The tip electrode is mounted on a micro-positioning system (Model Newport SMC100CC) and approaches a planar substrate in precise increments of ~20 nm. The entire setup is housed in an acrylic glove box that can be pumped to ~100 Torr and backfilled with a desired gas such as argon. The gap between the electrodes and subsequent breakdown of the gas is imaged by a camera system (Model Dino-Lite AM4115ZTL). Current-voltage (I-V) measurements are obtained at each gap by a programmable voltage supply and a current monitoring system.

Our results show that at small gaps of less than ~10 μm, the I-V curves exhibit a turn-on voltage, defined as the voltage where a current above the noise of ~100 nA is measured, followed by a non-linear, approximately exponential increase in current with applied voltage. The turn-on voltage is found to increase with gap from ~1-10 μm. Above ~10 μm, the non-linear regime is not observed and the I-V curve abruptly increases as a result of complete gas breakdown. To analyze the results, we have fitted the I-V curves at small gaps to Fowler-Nordheim theory, confirming that the current is produced from field emission. However, a major challenge is reproducibility of the data because of tip and substrate damage which continually affect field-emission behavior. We will discuss these issues and show our efforts to connect the experimental data to existing theory.

Keywords: microplasmas, field emission

11:00am **PS+SE-MoM9 Precise Energy and Temperature Measurements in Dielectric Barrier Discharges (DBD) at Atmospheric Pressure.**, *B. Nisol,* Groupe des Couches Minces (GCM) and Department of Engineering Physics, Polytechnique Montréal, Canada, *M. Archambault-Caron, H. Gagnon,* Groupe des Couches Minces (GCM) and Department of Engineering Physics, Polytechnique Montréal, *S. Lerouge,* Department of Mechanical Engineering, École de Technologie Supérieure (ETS), and Centre de Recherche du CHUM (CRCHUM), ***Michael Wertheimer***, Groupe des Couches Minces (GCM) and Department of Engineering Physics, Polytechnique Montréal, Canada

A specially designed dielectric barrier discharge (DBD) cell and associated equipment has been used to carry out precise measurements of electrical energy, E_g, dissipated per discharge cycle of the applied a.c. voltage, V_a, over the frequency range $5 \le f \le 50$ kHz. Twin pairs of several different dielectric materials (2.54 cm diameter discs, thicknesses = 2.0 or ca. 0.1 mm) with relative permittivities between $2.1 \le K' \le 9.5$ were used as dielectric barriers in DBDs of four different gases: He, Ne, Ar and N_2.

Much of the work relates to the study of atmospheric pressure glow discharge (APGD) plasma in flowing He gas; five separate thermometers (including fiber-optic probes immune to high voltage and high-frequency electromagnetic fields) have enabled us to perform a detailed calorimetric (heat balance) investigation in He APGD, believed to be the first of its kind. Fair agreement in the overall energy balance, which includes vacuum ultraviolet (VUV) light emission, lends strong support to the validity of both measurements and methodology. The latter includes refined algorithms that permit rapid data acquisition and processing. The present results are compared with literature, allowing several important conclusions / recommendations to emerge.

Next, we turn to the particular case of DBD in Ar in a pilot-scale reactor dedicated to deposition of thin organic films (PECVD) for biomedical applications. We have found that transfer of data from the small to the large (near 50-fold greater surface area) apparatus has been very successful, and that we can now precisely measure the amount of energy (ΔE_g) consumed in a particular PECVD process. We finish by presenting specific example reactions and link energy measurements with physico-chemical characteristics of deposits.

11:20am **PS+SE-MoM10 Plasma-Induced Conductivity in Dielectrics: A Study of Dielectric Barrier Discharges**, ***Floran Peeters****, FOM Institute DIFFER, Netherlands, *R.F. Rumphorst,* Eindhoven University of Technology, Netherlands, *M.C.M. van de Sanden*, FOM Institute DIFFER, Netherlands

In plasma devices, the surfaces bounding the plasma form an integral part of the system. Despite this, surfaces are generally described as perfect absorbers for electrons and ions, without any further consideration of potentially relevant processes taking place within the material. Dielectric surfaces, for instance, are treated as single capacitive elements, providing a wall potential. For most discharges this model is sufficiently accurate, but if the characteristic dimensions of dielectric and plasma are very dissimilar, such as in etched micro- and nanostructures or if the discharge itself is non-uniform, understanding the build-up of surface charges and their subsequent behavior becomes of paramount importance.

In our work, we use a typical non-uniform discharge to investigate the plasma-dielectric interaction: the dielectric barrier discharge (DBD) in filamentary mode. Filamentary DBDs can be described by an equivalent circuit which assumes discharging occurs uniformly across the surface, i.e. by treating the dielectric as a single continuous capacitive element. This is counter-intuitive, since DBD actually consists of many spatially and temporally separated, transient microdischarges. Studying the electrical characteristics of DBDs more closely, using both conventional *Q-V* diagrams combined with a circuit designed to record the transferred charge per filament, we developed an improved electrical model of the DBD. An extension to the electrical model for DBDs introduced by Manley in 1943, our model explicitly takes into account the localized nature of the discharge. Using this model, we find that individual filaments are always roughly equivalent; irrespective of the phase or amplitude of the applied voltage. We show that this leads to limited control over the chemical processing efficiency of DBD. The fundamental cause of the insensitivity of the discharge to the applied voltage is identified as the constant redistribution of surface charge on the dielectric.

Further investigation reveals that this redistribution of charge does not occur via the gas-phase of the residual plasma, as is often assumed, but is likely the result of excess charge carriers being introduced into the dielectric by the discharge. We provide corroborative evidence that these excess charge carriers, involving free electron and hole densities not normally seen in high-band gap materials, provide a boost to the conductivity of the material in locations affected by the plasma. As shown here for a DBD, this plasma-induced conductivity can have a significant effect on the behavior of the discharge and should be considered in any models of plasma involving dielectric surfaces.

11:40am **PS+SE-MoM11 Fabrication of Flexible, Electrically-Conductive Features by Microplasma Reduction of Cation-Cross-Linked Polyacrylic Acid (CCL-PAA) Films**, ***Souvik Ghosh§***, *R. Yang, P.X.-L. Feng, C.A. Zorman, R.M. Sankaran*, Case Western Reserve University

Patterned metal formation on substrates is typically achieved by subtractive methods. Recently, additive manufacturing techniques have emerged that can selectively deposit materials to produce patterned structures. Examples of additive methods include ink-jet, aerosol, and screen printing. A common feature of all of these approaches is the ink, a solution of stabilized colloidal metal nanoparticles that is deposited onto an arbitrary substrate. Removal of the organic stabilizers is often carried out by annealing at high temperatures (>200 °C) to produce electrically conductive features, limiting what substrates can be used. There are also challenges with deposition of the inks associated with the viscosity and adhesion of the inks to the substrate.

An alternative approach to fabricating patterned metals in polymers is *in situ* reduction of metal containing polymers. Here, we present an atmospheric-pressure microplasma process for the selective reduction of metal ions in polymer films to produce flexible, electrically-conductive metal patterns [1]. The films are made from polyacrylic acid (PAA) which reversibly cross links with metal cations such as silver (Ag^+). The films are subsequently exposed to a microplasma formed in a flowing argon gas on a two-dimensional scanning stage to "write" a desired pattern. Characterization of the films by X-ray diffraction (XRD) confirms that the Ag^+ is reduced to crystalline Ag after exposure to the microplasma. Further materials analysis by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDX) show that reduction leads to the formation of Ag nanoparticles whose size and morphology depend on the exposure conditions (i.e. plasma current, scanning rate, etc.). Cross-sectional characterization of the films shows that the reduction does not penetrate through the film bulk. We suggest that the Ag^+ diffuses to the film surface during reduction, leading to a near-surface layer of reduced crystalline Ag with bulk resistivity ~1 mΩ-cm. Stretchable films have been produced by casting PAA-Ag^+ films on top of a polydimethylsiloxane (PDMS) substrate, followed by exposure to the microplasma. Dynamic mechanical analysis (DMA) of the multilayer films yield a breaking force value of >3 MPa and the films can be stretched to >100%. Electrical measurements are performed on the films as a function of strain to analyze the change in resistivity with stretching. We will also present our recent efforts to reduce the size of the patterns, which is currently ~100 μm, to approximately 10 μm by incorporating stencil masks.

[1] S. Ghosh *et al.*, ACS Appl. Mater. Interfaces **6**, 3099 (2014).

Plasma Science and Technology
Room: 210B - Session PS-MoM

Advanced FEOL/Gate Etching
Moderator: Chanro Park, GLOBALFOUNDRIES

8:20am **PS-MoM1 FEOL Patterning Challenges for Sub 14nm FDSOI Technology**, ***Sébastien Barnola***, *N. Posseme, P. Pimenta-Barros, C. Vizioz,* CEA, LETI, MINATEC Campus, France, *C. Arvet,* ST Microelectronics, France, *O. Pollet, A. Sarrazin,* CEA, LETI, MINATEC Campus, France, *M. Garcia-Barros,* ST Microelectronics, France, *L. Desvoivres*, CEA, LETI, MINATEC Campus, France **INVITED**

Fully-depleted SOI devices (FDSOI) are proven to provide excellent control of gate electrostatics. This makes them a real solution to meet performance requirements down to 10nm technology node, however new architectures such as stacked silicon nanowires will be required to maintain low leakage current when further downscaling gate length. Additionally new materials are required to build transistor channel complying with ON-state current expectations, such as new channel materials such as germanium or compound semiconductors or low k materials at the spacer level.

These changes in transistor integration raise quite a number of new challenges for etching and stripping in that they introduce new materials with uncommon properties compared to usual silicon-based devices.

Another challenging aspect of device downscaling is the enhanced demand for high-selectivity etch. In spacer definition for instance, maximum allowable silicon recess in source / drain regions is less than 0.5nm for the 14nm node. To this end new techniques are being developed that involve a prior modification of the etched layer down to a controlled depth, followed by the removal of the modified layer selectively to the non-modified material.

On the technology side, immersion 193nm lithography has reached its limits in resolution and the most critical levels require costly dual or quad-patterning technique to achieve stringent CD specifications in current 14nm and beyond. Solutions to further expand 193nm lithography capabilities at lower costs are showing promising results, such as sidewall image transfer (SIT) or directed self-assembly (DSA). Nevertheless these newly developed techniques involve process adaptations on the plasma etching side since they induce changes in the masking materials.

*** Coburn & Winters Student Award Finalist**

9:00am **PS-MoM3 Material and Etch Interaction Comparisons for SIT Patterning**, ***John Sporre,*** IBM Corporation*, A. Raley,* TEL Technology Center, America, LLC*, D. Moreau,* STMicroelectronics*, M. Sankarapandian, P.K.C. Sripadarao, J. Fullam, M. Breton, R. Chao, S. Kanakasabapathy,* IBM Corporation*, A. Ko*, TEL Technology Center, America, LLC

Sub-Lithographic pitch patterning requires advanced patterning techniques capable of achieving reduced dimensions with current lithography technology. Novel techniques are employed to pattern gates with critical dimensions below the current resolution limits of optical lithography. One such technique is Sidewall Image Transfer (SIT), where the critical dimension of the gate is established by the controlled deposition of a spacer on top of a Lithographically defined mandrel. The material selection of the mandrel and spacer materials can influence the functionality of the SIT process, and this paper specifically compares the use of an ashable organic mandrel to an inorganic mandrel. Organic mandrels for mandrel removal selective surrounding spacer material. However inorganic mandrels, are resistant to profile modifications. In this paper, we compare both approaches with specific focus on the influence of plasma etch chemistries on mandrel profile characteristics.

9:20am **PS-MoM4 Trim Etch for sub-20 nm Technology***,* ***Guangjun Yang****, D. Keller, Y. Rui, R. Benson, A. Schrinsky*, Micron Technology

Photo resist trim with isotropic etch is a common practice in industry for CD control and line width roughness (LWR) improvement for sub 35 nm features imaged with 193nm lithography. As CD shrinks further, it becomes more challenging to control CD, to reduce line buckling or wiggling and to manipulate etch profile. For CDs below 20 nm, hardmask trim and live structure trim play an important role. In this talk, we will present a few examples of isotropic trim for sub-20 nm technology using mainly ICP chambers. In one case, DUV photo resist was trimmed from 40 nm to 15 nm with good LWR and good remaining height. In another case, a Si3N4/metal stack was trimmed down to 8 nm from 15 nm with good SWR (space width roughness) and etch profile. In the third case, we selectively trim DLC (diamond-like-carbon) in the bottom portion of the profile to make the etch profile straighter. Also we will discuss some challenges in developing a good isotropic trim process such as trim etch selectivity to materials and to location, etch uniformity. Finally we will discuss some opportunities for etch tool development.

9:40am **PS-MoM5 Laser-Assisted Dry Etch of poly-Si and SiO_2 for Semiconductor Processing***,* ***Jason Peck****, G.A. Panici, I.A. Shchelkanov, D.N. Ruzic*, University of Illinois at Urbana-Champaign

Dry etch assisted by laser (DEAL) of silicon and silicon dioxide via $Ar/SF_6/C_4F_8/O_2$ capacitively-coupled plasma was studied, with goals including form control for sub-22 nm features and uniformity for 450 mm wafer processes. The first phase of the work confirmed the feasibility of the proposed concept. The second phase of the work was focused on pulse frequency, length and wavelength influence on etching rate. Two lasers with different repetition rates, wave lengths and pulse widths were used. The first one is a (2.5 – 7 ns FWHM) Nd:YAG laser with repetition rate of 100 Hz. The Nd:YAG laser was capable to produce emission at 1064, 532 and 266 nm wavelengths. The second laser was a 1043 nm IMRA laser with 300 fs pulses and 1 MHz pulse rate. Continuous wave (CW) laser systems were also tested.

The etch rate enhancements were determined. The predominant laser-assisted etch mechanism was interpreted to be electrochemical, with electron-hole pairs catalyzing chemical etching at the surface. The influence of laser repetition rate was studied in both SF_6 and C_4F_8 etch. The beam intensity profile influence onto etch pattern was studied. In all cases, an emphasis on low power density kept the experiments well under the ablation threshold, minimizing pyrolytic damage by the incident beam. Impact on current industry processes will be discussed.

10:00am **PS-MoM6 Spatial Resolution Considerations for Uniformity Improvement by Gas Cluster Ion Beam Etch***,* ***Joshua LaRose,*** TEL Technology Center, America, LLC*, B. Pfeifer, V. Gizzo,* Tokyo Electron*, N. Joy, N.M. Russell*, TEL Technology Center, America, LLC

Abstract

Sub-14nm CMOS requires a demanding level of integrated thickness control at several critical layers in the fabrication process in order to meet functional and parametric yield/Cpk goals. Gas cluster ion beam (GCIB) etching is becoming increasingly adopted to meet this need by using precise corrective etching with location specific processing (LSP) to meet within-wafer and wafer-to-wafer control requirements. LSP etch correction may be driven by any input map delivered to the tool via factory automation, or may be driven by on-board integrated metrology. In either case the extent to which a uniformity pattern can be corrected may be limited by the length scale of non-uniform features as compared to the size of the beam, and the ability of the metrology sampling plan to resolve the features. Here we characterize in some detail, the influence of sampling density and non-uniformity length scale on LSP resolution capability.

LSP was able to substantially reduce the standard deviation of a model incoming non-uniformity map for features with > 8 mm length scale, and to adequately resolve such features, requires a metrology sampling plan corresponding to > 89 points on a 300 mm wafer. For wafer-edge non-uniformity, we show similar capability to resolve features > 10 mm by LSP, with sufficient metrology sampling density, and introduce a hybrid edge model scheme that can enable improved resolution of edge features with as few as 37 metrology points. Here we describe in detail the techniques used to determine the resolution performance, summarize results from several relevant cases, and present clear guidelines on sampling strategies for LSP etching.

10:40am **PS-MoM8 Analysis of Surface Reaction Layers formed by Highly Selective Etching with Pulsed Microwave Plasma***,* ***Miyako Matsui,*** Hitachi Ltd., Japan*, M. Morimoto, N. Ikeda, T. Ono*, Hitachi High-Technologies Corp. **INVITED**

Three dimensional (3D) transistors, such as a Fin-FET, have increasingly necessitated etching processes with higher selectivity and greater anisotropy. For example, a Si_3N_4 spacer layer needs to be anisotropically etched with a vertical profile without leaving residue on the sidewalls of the fins while keeping high selectivity in regard to Si fins. To provide more highly selective and more anisotropic etching for fabricating next-generation 3D devices, an etching system combining a pulsed-microwave ECR plasma and time-modulated wafer bias was developed.

In this study, the mechanism of highly selective etching with a pulsed-microwave ECR plasma was investigated by analyzing surface-reaction layers formed on etched materials. To clarify the etching mechanisms of poly-Si, Si_3N_4, and SiO_2, surface-reaction layers formed not only on unpatterned surfaces but also at the bottoms of line-and-space patterns were analyzed by XPS. Specimens were etched using an $HBr/O_2/Ar/CH_4$ gas chemistry for poly-Si etching and using a $CH_3F/O_2/Ar$ gas chemistry for Si_3N_4 etching. The XPS results revealed that a modified layer formed on all etched materials and that a polymer layer formed on the modified layer. To determine the effects of the etching parameters on etching selectivity, the thickness and composition of the reaction layers, which were the polymer layer and the modified layer, were quantitatively analyzed. To examine the thermal reactivity between the reaction layers and the etched materials, etched surfaces were analyzed by TDS.

Highly selective etching mainly originated from the difference in the thickness of the polymer layers that formed on the etched materials under the pulsed plasma. The thickness of the polymer layer was controlled so that etching did not stop even at a low wafer bias voltage. Reactivity between the reaction layers and the etched material was controlled by adjusting the composition of the reaction layers. Especially in the case of Si_3N_4 etching, the N in the Si_3N_4 layer thermally reacted with the reaction layers, forming NH_3 or HCN, and the Si in the Si_3N_4 layer had high reactivity with the F in the reaction layers. Due to the high reactivity between the F-rich reaction layers and the Si_3N_4 layer caused by the pulsed plasma, the polymer layer became thin even at a low wafer bias and thus promoted ion-assisted etching. As a result, wide process windows were provided by formation of the reaction layers under the pulsed plasma.

11:20am **PS-MoM10 Improvement of Gate Shoulder Retention and SiN Selectivity over Si in Spacer Process***,* ***Yohei Ishii****, K. Okuma, N. Negishi, J. Manos*, Hitachi High Technologies America Inc.

To achieve improvements in semiconductor device performance, 3D transistors (FinFET) were introduced due to limitations in planar structures. Because of the complexity of the structure and high aspect ratio features, new challenges have appeared. Among many processes, spacer etch is one process that could have an impact on device performance. During spacer etch, there are several issues that arise such as SiN selectivity over Si and gate shoulder retention.

In this presentation, we will demonstrate a spacer etching process, using a novel gas, and utilizing a Hitachi microwave Electron Cyclotron Resonance (M-ECR) etcher. SiN selectivity over Si is improved compared to a conventional gas chemistry such as CH3F base process. In addition, while the spacer is etched, the gate shoulder has to be protected. Finally, we will also introduce an etching method that overcomes the trade-off relationship between gate shoulder retention and spacer etch.

11:40am **PS-MoM11 Advanced Patterning Applications Using High Selectivity Etch Chemistry**, ***Nathan Marchack**, S.U. Engelmann, E.A. Joseph, R.L. Bruce, H. Miyazoe, E.M. Sikorski,* IBM T.J. Watson Research Center*, T. Suzuki, M. Nakamura, A. Itou,* ZEON Chemicals L.P.*, H. Matsumoto*, Zeon Corporation, Kawasaki, Japan

Image reversal has been utilized in semiconductor manufacturing to invert line/space [US6221562 B1] and hole/pillar [US6358856 B1] patterns. Since this process requires the ability to remove one material with high selectivity to another, traditionally either contrasting dielectrics (such as SiN/SiOx) or complementary types of photoresist (e.g. positive/negative tone) have been used. While carbon-based soft materials are easier to deposit than dielectric films, lack of selectivity and physical integrity can potentially hinder successful image reversal processes when they are combined with hard materials, e.g. metals, dielectrics.

We present an image reversal process by depositing an organic planarizing layer (OPL) material into a hole array patterned in SiN to create pillars, which are a commonly required shape for a variety of emerging technologies. By using a gas chemistry with an extremely high selectivity to OPL, plasma etch removal of the SiN is possible, allowing pattern fidelity to be maintained at pitches below 100nm. We demonstrate control of the pillar CD by controlling the time of the OPL etchback step.

For applications requiring minimal mask budget, we utilize the same chemistry's selectivity to SiOx to demonstrate patterning of SiN hard mask features with reduced LER/LWR and iso/dense loading ratio. We demonstrate hard mask patterning of 80nm thick SiN with 35nm SiOx hard mask for 50nm pitch lines, with potential applications for advanced technology nodes. The results were achieved in both RLSA and ICP plasma sources.

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic
Room: 112 - Session SA-MoM

Imaging and Nanodiffraction (8:20-10:00 am) & Novel Insights in Correlated Materials, Organic Materials and 2D Solids (10:40 am -12:00 pm)
Moderator: Herrmann Dürr, Stanford University, Petra Rudolf, University of Groningen

8:20am **SA-MoM1 Nanoscale Chemical Imaging by Soft X-ray Spectro-microscopy and Spectro-ptychography**, ***Adam Hitchcock**, X.H. Zhu,* McMaster University, Canada*, J. Wu,* McMaster University*, D. Shapiro, T. Tyliszczak*, Lawrence Berkeley Lab, University of California, Berkeley **INVITED**

Recent improvements in instrumentation and data analysis for soft X-ray spectromicroscopy and spectro-ptychography have made significant advances in spatial resolution and sensitivity. These improvements are providing researchers with new tools to contribute to solving real world technological issues as well as making fundamental discoveries. This presentation will give an overview of the performance of current instrumentation, report on exciting advances taking place in soft X-ray spectro-ptychography, and outline opportunities for *in situ* and *operando* studies. Spectro-ptychography studies of the magnetism of individual magnetosomes in magnetotactic bacteria by X-ray magnetic circular dichroism (XMCD). Results for 2D and 3D chemical analysis of polymer-electrolyte fuel cells will be presented.

Research performed at the Advanced Light Source, funded by DoE, BES, and at the Canadian Light Source, funded by CFI, NSERC, U. Saskatchewan, Saskatchewan, WEDC, NRC and the CIHR. The SHARP code used for ptychographic data analysis was developed by the Center for Applied Mathematics for Energy Research Applications (CAMERA) at LBNL, led by Jamie Sethian, in collaboration with Uppsala University .

9:00am **SA-MoM3 Imaging Single Cells in a Beam of Live Cyanobacteria with an X-ray Laser**, ***Gijs van der Schot***, Uppsala University, Sweden **INVITED**

Imaging live cells at a resolution higher than achieved using optical microscopy is a challenge. Ultra-fast coherent diffractive imaging[1] with X-ray free-electron lasers (XFELs) has the potential to achieve sub-nanometer resolution on micron-sized living cells[2]. Our container-free injection method can introduce a beam of live cyanobacteria into the micron-sized focus of the Linac Coherent Light Source (LCLS) to record diffraction patterns from individual cells, with low noise at high hit rates[3]. We used iterative phase retrieval[4-6] to derive two-dimensional projection images directly from the diffraction patterns. Synthetic X-ray Nomarski images[7], calculated from the complex-valued reconstructions, show cells in a similar manner to what one would expect to see using a Nomarski microscope, only at higher resolution than currently available. In a first experiment, we collected diffraction patterns to 33-46 nm full-period resolution, and reconstructed the exit wave front to 76 nm resolution[3]. In a second experiment, we demonstrate that it is indeed possible to record diffraction data to nanometer resolution on live cells with an intense, ultra-short X-ray pulse as predicted earlier[2,3]. These results are encouraging, and future developments to the XFELs and improvements to the X-ray area-detectors will bring sub-nanometer resolution reconstructions of living cells within reach.

We thank the Swedish Research Council, the Knut and Alice Wallenberg Foundation, the European Research Council, the Röntgen-Ångström Cluster, and Stiftelsen Olle Engkvist Byggmästare for supporting this work.

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10:00am **SA-MoM6 Nanoscale Tomography and Spectroscopy with the HZB X-ray Microscope**, ***Gert Schneider***, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Germany

The Helmholtz-Zentrum Berlin (HZB) operates a full-field transmission X-ray microscope (TXM) at the BESSY II electron storage ring. The advanced optical setup of the HZB-TXM permits NEXAFS spectroscopic applications as well as correlative fluorescence and nanoscale tomographic imaging of cryogenic fixed cells in a fully hydrated state. An overview of recent results in material and life sciences will be presented [1-8]. Investigations on TiO2 nanostructures using NEXAFS spectromicroscopy at the Ti-L- and O-K-absorption edges will be shown [1,2]. Additionally, first results on the nanoscale morphology of organic solar cells will be discussed. Reconstructions taken from 3D X-ray datasets allow to visualize sub-cellular ultrastructures in mammalian and plant cells e.g. algae. Quantitative studies as e.g. the number of cell organelles in the cell volume are possible [4]. Scientific findings on the nucleation of hemozoin in Plasmodium falciparum by nanoscale tomography with the HZB-TXM will be demonstrated [5]. Studies of the interaction of viruses like the Herpes virus [6] or vaccinia virus [7] with mamillian cells will be presented. In addition, nanoscale X-ray tomography paves the way to a better understanding of the interaction of nanoparticles with cells [8].

[1] P. Guttmann et al., Nature Photonics 6 (2012), 25-29

[2] K. Henzler et al., Nano Letters 13 (2013), 824-828

[3] G. Schneider et al., Nature Methods 7 (2010), 985-987

[4] E. Hummel et al., PLoS ONE 7 (12) (2012), e53293

[5] S. Kapishnikov et al., PNAS (2012) DOI: 10.1073/pnas.1118120109

[6] C. Hagen et al., J. Struct. Biol. 177 (2012), 193-201

[7] FCO J. Chichon et al., J. Struct. Biol. 177 (2012), 202-211

[8] D. Drescher et al., Nanoscale 5 (2013), 9193-9198

10:40am **SA-MoM8 Exploring All-optical Magnetic Switching with Resonant X-rays**, ***Alexander Reid***, SLAC National Accelerator Laboratory **INVITED**

The ability to write a magnetic `bit', a stable magnetic domain, with a single sub-picosecond optical pulse is now known and demonstrated in magnetic materials from amorphous ferrimagnets, such as GdFeCo, to crystalline ferromagnets, such as FePt. However, understanding the underlying physics of this process remains a fundamental challenge in magnetism dynamics. The process of all-optical switching of magnetization begins with the absorption of the optical pulse by the magnetic material, this creates a highly non-equilibrium state. The evolution of this state is controlled by many factors, from fundamental coupling interactions to material heterogeneity. Resonant x-rays allow a powerful tool for exploring the evolution of this non-equilibrium state and beginning to answer questions about how and why reversed magnetic order can emerge deterministically. Powerful new x-ray sources, such and the Linac Coherent Light Source, produce femtosecond x-ray pulses with a high spatial coherence and brightness. Using such sources, and techniques such as x-ray circular magnetic dichroism, the transient elemental magnetism can be monitored during the switching process. Further, the intrinsically shorter wavelength of x-rays enables monitoring of the spatial aspects of the switching process down to length scales of a few nanometers. We detail recent measurement of the spatio-temporal dynamics of the switching process in the prototype materials GdFeCo and TbFeCo, which have led to new insights about the evolution of the optical magnetic switching process.

11:20am **SA-MoM10 Ultrafast Dynamics in Magnetic Systems**, ***Gerhard Gruebel***, Magnetic Dynamics, Germany **INVITED**

Ultrafast Dynamics in Magnetic Systems

Gerhard Grübel

DESY and The Hamburg Centre for Ultrafast Imaging (CUI)

Hamburg, Germany

Understanding ultrafast magnetization Dynamics on the nano-scale is a forefront problem in modern magnetism research with direct impact on the quest for faster and smaller storage devices. Probing the magnetization element-specifically and on the nanometer lenght-scale is a pre-requisite when probing technologically relevant material systems with complex composition.

X-ray free electron laser (FEL) sources with their unique properties delivering ultrashort and super intense soft X-ray pulses allow for the first time to address magnetization dynamics on the relevant time-and lenght scales.

We present recent results obtained on multi-domain Co/Pt magnetic multilayer samples with perpendicular magnetic anisotropy, pumped with short IR and THZ pulses. As a probe we use small angle X-ray scattering from the magnetic domains which, via X-ray magnetic circular dichroism at the Co M-edge, allows us to simultaneously obtain information on the magnitude of the local magnetization amd the characteristic lenght scale of the domains. The FEL sources FLASH at DESY (Hamburg) and FERMI at ELECTRA (Trieste) were used at a wavelenght of 20.8 nm corresponding to the CO M-edge.

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 Mo_2BC 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.

[1] D. G. Sangiovanni, D. Edström, L. Hultman, V. Chirita, I. Petrov, and J. E. Greene, "Dynamics of Ti, N, and TiNx (x=1–3) admolecule transport on TiN(001) surfaces," *Phys. Rev. B*, vol. 86, no. 15, p. 155443, 2012.

[2] D. Edström, D. G. Sangiovanni, L. Hultman, V. Chirita, I. Petrov, and J. E. Greene, "Ti and N adatom descent pathways to the terrace from atop two-dimensional TiN/TiN(001) islands," *Thin Solid Films*, vol. 558, pp. 37–46, 2014.

[3] D. G. Sangiovanni, D. Edström, L. Hultman, I. Petrov, J. E. Greene, and V. Chirita, "Ab initio and classical molecular dynamics simulations of N_2 desorption from TiN(001) surfaces," *Surf. Sci.*, vol. 624, pp. 25–31, 2014.

[4] D. G. Sangiovanni, D. Edström, L. Hultman, I. Petrov, J. E. Greene, and V. Chirita, "Ti adatom diffusion on TiN(001): Ab initio and classical molecular dynamics simulations," *Surf. Sci.,* vol. 627, pp. 34-41, 2014.

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$_3$)$_3$B**, ***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$_3$)$_3$B (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 ^{o}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 ^{o}C, 100-textured WC$_{1-x}$ films are deposited and with a shift to a weak 111 orientation at lower temperatures. At 500 ^{o}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 ^{o}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$_2$O$_3$(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$_2$O$_3$(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$_2$O$_3$(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)$_2$O$_3$-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.

Surface Science
Room: 113 - Session SS+AS+EN-MoM

Synthesis, Structure and Characterization of Oxides
Moderator: Sylvie Rangan, Rutgers, the State University of New Jersey

8:20am **SS+AS+EN-MoM1 Oxygen Uptake on Rh(111)**, ***Daniel Killelea***, *J. Derouin, R.G. Farber*, Loyola University Chicago

Rhodium surfaces are of high utility for the partial oxidation of small molecules. We present results from a study of the uptake of gas-phase oxygen atoms on the Rh(111) surface. A combination of temperature programmed desorption (TPD), Auger electron spectroscopy (AES), and scanning tunneling microscopy (STM) were used to determine the total amount of oxygen, the oxygen surface coverages, and the surface structures, respectively. Our findings suggest that oxygen atoms are readily incorporated in to the near-surface region on Rh(111) while retaining low oxygen surface coverages and structures. We further studied how the surface changes when the subsurface oxygen atoms emerge to the surface. These finding provide insight to the formation of bulk oxides, and show that high-coverages of oxygen are not necessary for absorption of oxygen into the selvedge.

8:40am **SS+AS+EN-MoM2 Formation of Subsurface Oxygen and Surface Oxides on Ag(111) by Atomic Oxygen**, ***Jonathan Derouin****, *R.G. Farber, D.R. Killelea*, Loyola University Chicago

Understanding the interaction of oxygen with transition metal surfaces is important in many areas including corrosion and catalysis. The oxygen/silver system in particular has been studied extensively both experimentally and theoretically. Interest is driven largely by the role of silver in two widely used industrial reactions: the epoxidation of ethylene to produce ethylene oxide and the partial oxidation of methanol to produce formaldehyde. In addition, the oxygen/silver system can serve as a model for the dissociative chemisorption of diatomic molecules on close packed metal surfaces. Despite extensive research, the oxygen/silver system is still not well understood. To better understand this system, we use UHV-STM, AES and TPD to study the adsorption of atomic O on an Ag(111) crystal. Atomic O is generated by thermally cracking molecular O. By varying the power of the thermal cracker we are able to change the flux of atomic O reaching the Ag surface. Higher atomic O fluxes produce O structures which desorb at significantly higher temperatures than structures produced with lower O fluxes. We then use UHV-STM to further characterize the various oxide structures produced.

9:00am **SS+AS+EN-MoM3 Surface and Bulk Properties of Pure and Mixed Titania**, ***Matthias Batzill***, University of South Florida **INVITED**

Titanium oxide in its different polymorphs remains a model system for structure property relationships in simple oxides. In this talk we address issues related to both the bulk and the surface properties of TiO2. Measuring the photocatalytic activity of anatase- and rutile- epitaxial films we conclude that charge carriers excited deeper in the bulk contribute to the surface photocatalytic activity for anatase compared to rutile [1]. This difference may be an important factor for explaining the generally higher photocatalytic activity of anatase-TiO_2. In the second part of the talk, surface properties are presented on the example of rutile TiO_2(011). The (011) surface orientation is less frequently studied compared to the (110) surface. Under UHV-conditions the (011) surface reconstructs into a complex 2x1 structure. We investigate the stability of this reconstruction under chemical adsorption. We find that for strongly adsorbing molecules the surface restructures to enable stronger adsorption. We show that this restructuring is strongly anisotropic resulting in quasi-1D adsorbate structures [2]. The instability of the rutile TiO_2(011)-2x1 surface may also be exploited for the formation of unique mixed oxide surfaces. This we demonstrate with iron oxide, which forms an ordered mixed TiFeOx surface oxide layer. Such mixed oxide surface may also form by impurity segregation from the bulk and thus may be a common surface structure in Fe-doped TiO_2.

[1] "Why is anatase a better photocatalyst than rutile? - Model studies on epitaxial TiO_2 films" T. Luttrell, S. Halpegamage, J.G. Tao, A. Kramer, E. Sutter, M. Batzill Sci. Rep. 4, 4043 (2014).

[2] "Adsorbate Induced Restructuring of TiO_2(011)-(2×1) Leads to One-Dimensional Nanocluster Formation" Q. Cuan, J. Tao, X.Q. Gong, M. Batzill Phys. Rev. Lett. 108, 106105 (2012).

9:40am **SS+AS+EN-MoM5 Characterizations of Non-polar Polar Interfaces: Cr_2O_3 on ZnO (0001) and (000-1)**, ***Xiaodong Zhu***, *M.D. Morales-Acosta, J. Shen, F.J. Walker, J. Cha, E.I. Altman*, Yale University

The growth of non-polar Cr_2O_3 on oppositely poled ZnO surfaces was characterized to determine how the polar substrate influences the properties of the non-polar film. Photoelectron spectroscopy (XPS and UPS), electron diffraction (RHEED and LEED), High-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD) and X-ray reflectivity (XRR) have been performed to determine the growth mode, film quality and interfacial electronic properties are influenced by the substrate polarization. The growth is 2D; however, the films appear initially disordered on both substrates. With increasing film thickness, the films ordered with a well-defined epitaxial relationship. The HRTEM and XRD/XRR results for thicker films confirm a clear interface and well-defined lattice structure near the interface and throughout the film, indicating that above a critical thickness the entire film reorganizes into an ordered structure. The polar interfaces show a small but noticeable band offset that decayed with increasing film thickness. Statistical analysis of UPS valence band spectra revealed an enhanced density of states near the Fermi level for Cr_2O_3 on the positive surface consistent with stabilization of the positive interface by charge transfer; in contrast, no significant valence band differences were observed between bulk Cr_2O_3 and thin Cr_2O_3 thin layers on the negative surface. The results will be compared with those obtained for ZnO/Cr_2O_3/ ZnO (0001) and (000-1) to determine if the interfacial properties are sensitive to how the interface is formed.

10:40am **SS+AS+EN-MoM8 Exploring Iron Oxide Clusters and Films Supported on HOPG with HREELS and AES**, ***Joel Langford***, University of California, Irvine, *F. Rosner,* Technical University of Munich, Germany, *J. Kwon, J.C. Hemminger*, University of California, Irvine

We are using High Resolution Electron Energy Loss Spectroscopy (HREELS) and Auger Electron Spectroscopy (AES) to investigate nanoclusters and films of iron oxide supported on highly oriented pyrolytic graphite (HOPG). For the films, two AES oxidation profiles were generated by annealing in oxygen. One profile was at a constant sample temperature of 500 K with varying exposure, the other by varying sample temperature while keeping exposure at a constant 1000 L. Both oxidation profiles

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*** Morton S. Traum Award Finalist**

saturate at an AES O/Fe ratio of 1.2. This ratio is below the O/Fe ratio of magnetite (Fe_3O_4), and hematite (Fe_2O_3) indicating incomplete oxidation of the film. Additional evidence for incomplete film oxidation comes from the absence of Fuchs-Kliewer phonons in the HREEL spectra. For the nanoclusters we are investigating two systems; polydispersed iron oxide nanoclusters on HOPG, and platinum nanoclusters supported on iron oxide nanoclusters. The polydispersed nanoclusters are more susceptible to oxidation than the film as evident by the higher AES O/Fe ratio and the presence of Fuchs-Kliewer phonons in the HREEL spectra. The platinum nanoclusters are synthesized on the iron oxide nanoparticles by an ex-situ photodeposition technique and therefore adventitious carbon is adsorbed prior to transfer into the UHV chamber. To remove the adventitious carbon we annealed in oxygen at a sample temperature of 1000 K. HREEL spectra show that the annealing procedure removes adventitious carbon because of the absence and appearance of a CO resonance before and after cleaning, respectively. HREEL spectra after low temperature CO adsorption and as a function of subsequent anneal temperature will be presented.

11:00am **SS+AS+EN-MoM9 Computational Materials Design®: Ionic Conduction in Rare-Earth-Metal Oxides from the First Principles-based Studies**, ***Susan Aspera***, *M. Sakaue, M. Alaydrus, T.P.T. Linh, N.H. Linh, H. Nakanishi,* Osaka University, Japan, *H. Kasai*, Akashi College, Japan

Solid oxide fuel cells (SOFC) have been one of the most promising technologies to tap alternative sources of energy. This technology utilizes abundant fuel materials such as H_2, CH_4 and other hydrocarbon materials to lessen our dependence on non-renewable fossil fuels that are nearly depleting. It takes into advantage the efficiency brought about by high kinetics of reaction at the electrolyte sides occurring at high working temperature. With this, ceramic based materials are often used as electrolyte and electrode materials. However, the working temperature of SOFCs is often too high (700˚C to 1000˚C). This limits the application of SOFCs and consequently high cost of producing durable materials for high working temperature. Recently, research related to this technology focuses on materials that work at intermediate temperature (IT-SOFC). This entails finding/designing materials that have high ionic conductivity at IT-SOFC working temperature.

Recent developments in computational simulation techniques, coupled with the rapid progress in computer efficiency, make first principles-based COMPUTATIONAL MATERIALS DESIGN (CMD®) a relevant field in the world of surface science and condensed matter physics. In this scheme, quantum mechanical calculations are performed to design promising materials and, understand the necessary mechanisms for the realization of an efficient technological device. Here, we employed the CMD® process and density functional theory-based analysis to study the atomic and electronic properties of several rare-earth-metal oxides (Pr_2NiO_2, La_2GeO_5, $LaGaO_3$ and CeO_2) which has potential application in IT-SOFC. These materials are known to have different structures according to symmetry, and the mechanism by which O ion conducts, i.e. via oxygen vacancies (O_{vac}) migration or O interstitial migration. The O ion migration path is dependent on the structure of the material, and the corresponding activation energy barrier for oxygen ion migration (E_{ac}) is affected by the concentration of O_{vac} and the presence of dopants, for O ion conduction via vacancies. In most of these systems, dopants with the same ionic radius as the host materials create high probability for O_{vac}, which then affects ionic conductivity, and the E_{ac} is found to be least for dopants with ionic radius near to that of the host material. Furthermore, as ionic migration is sensitive to the atomic structure, E_{ac} is party due to the structural alteration brought about by the presence of impurities such as dopants and creation of heterostructure interfaces. With these understanding, we can comment on the methods by which ionic conductivity can be enhanced in these materials.

11:20am **SS+AS+EN-MoM10 Modeling and Characterization of Exemplar Sealing Glasses to Develop Chemistry-Structure-Property Relationships**, ***Michael Brumbach***, *T. Zeitler, T. Alam, M. Rodriguez, L. Criscenti, M. Kalan, A. Mirabal, D. Bencoe, K. Ewsuk*, Sandia National Laboratories

The performance of joining materials in many applications, such as glass-to-metal seals in solid oxide fuel cells and medical devices, require improvements in glass properties for greater reliability. In this work, simple sealing glass compositions have been used to develop experimentally-validated molecular models. The goal is to understand glass chemistry and structure such that modeling can be used to guide glass design, for manufacturability, and optimized performance. The coupled modeling and experimental work will be discussed.

Technological glasses are used in many applications where inorganic joining is required. Applications of joining glasses include glass in glass-to-metal seals (in solid oxide fuel cells or medical components), glass-bonded ceramics (such as debased aluminas), and low temperature co-fired ceramic (LTCC) packaging for microelectronics. For these applications, well-controlled processing conditions and high reliability in the end-product are of paramount importance. To better understand materials performance and reliability our objective is to develop experimentally-validated simulation tools to predict and control glass chemistry-structure property relationships. These tools will be used to predict structure-function relationships in bulk glasses and at joining interfaces.

Results from experimental characterization of several barium aluminosilicate glasses will be discussed. Solid-state NMR, lab-based and synchrotron X-ray scattering, and EXAFS have been used to determine structural characteristics of the exemplar glasses. Comparison of experimental results to molecular dynamics modeling of the three-component glass will be presented. Additional simulations of glass properties and comparisons to measurements will also be discussed.

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Thin Film
Room: 111 - Session TF+AS+SS-MoM

Self-Assembled Monolayers, Layer-by-Layer, etc.
Moderator: Han Zuilhof, Wageningen University, Netherlands

8:20am **TF+AS+SS-MoM1 The Effects of Embedded Dipoles in Aromatic Self-Assembled Monolayers**, ***Swen Schuster***, Universität Heidelberg, Germany, *T. Abu-Husein,* Universität Frankfurt, Germany, *D.A. Egger, I. Hehn,* Graz University of Technology, Austria, *M. Kind,* Universität Frankfurt, Germany, *E. Zojer,* Graz University of Technology, Austria, *A. Terfort,* Universität Frankfurt, Germany, *M. Zharnikov*, Universität Heidelberg, Germany

Self-assembled monolayers (SAMs) are frequently used as intermediate films to modify charge-carrier injection from metal-electrodes into an organic semiconductor. This is usually achieved by use of the terminal dipolar groups comprising the SAM-ambience interface and affecting, at the same time, the growth chemistry of the semiconductor. Here we suggest an alternative approach, viz. embedding dipolar element into the molecular backbone, which allows decoupling the dipole control and the interfacial chemistry. As molecular backbone we use oligophenyl moiety which provides a suitable structural match to most organic semiconductors. As polar unit we use pyrimidine, varying its orientation in the molecular backbone and, consequently, the direction of the embedded dipole moment. The electronic and structural properties of these embedded-dipole SAMs are thoroughly analyzed using a number of complementary characterization techniques combined with quantum-mechanical modeling. We show that such mid-chain substituted monolayers are highly interesting from both fundamental and application viewpoints, as the dipolar groups are found to induce a potential discontinuity inside the monolayer, electrostatically shifting the energy levels in the regions above and below the dipoles relative to one another. These SAMs also allow for tuning the substrate work function in a controlled manner independent of the docking and interfacial chemistry. In addition, a mixture of the embedded-dipole molecules with opposite orientations of dipoles makes possible a fine tuning of the work function between the ultimate values, associated with a particular dipole orientation. Quantum-mechanical modeling in conjunction with x-ray photoelectron spectroscopy experiments provides insight into the molecular organization of such mixed monolayers.

8:40am **TF+AS+SS-MoM2 IR Spectroscopic studies of Molecular Thin Films exhibiting Spontaneous Dipole Alignment**, ***Alexander Rosu-Finsen***, Heriot-Watt University, UK, *J. Lasne,* Heriot-Watt University, France, *A. Cassidy, D. Field,* Aarhus University, Denmark, *M.R.S. McCoustra*, Heriot-Watt University, UK

In recent years, observations of the presence of a spontaneous and powerful static electric field within thin films of molecular solids have been reported by Field and co-workers [1]. These electric fields, which can approach 10^8 V m^{-1} or more, are believed to arise from alignment of the molecular dipoles in the thin films. Seeking to provide an independent means of observing this phenomenon of the "spontelectric phase", the first new electrically-unique, structural phase to have emerged in decades, we have used reflection-absorption infrared spectroscopy (RAIRS) to investigate thin films of nitrous oxide (N_2O). The presence of a static electric field within the thin film, the defining characteristic of spontelectrics, is demonstrated through the observed temperature dependence of longitudinal-transverse optical

(LO-TO) splitting in RAIR spectra, using an analysis based on the vibrational Stark effect [2]. Tentative evidence for the surface-templating of the growth of the spontelectric phase will be presented from RAIRS studies of solid carbon monoxide (CO) on a range of water substrates (porous amorphous solid water, compact amorphous solid water and crystalline water) [3].

[1] Spontaneous electric fields in solid films: spontelectrics. D. Field, O. Plekan, A. Cassidy, R. Balog, N.C. Jones and J. Dunger, *Int. Rev. Phys. Chem.*, 2013, **32**, 345-392.

[2] Spontaneously electrical solids in a new light. J. Lasne, A. Rosu-Finsen, A. Cassidy, M. R. S. McCoustra and D. Field, *Phys. Rev. Lett.*, submitted.

[3] Templating dipole alignment in solid carbon monoxide on water ice surfaces. A. Rosu-Finsen, J. Lasne, A. Cassidy, D. Field and M. R. S. McCoustra, *Phys. Rev. Lett.*, in preparation.

9:00am **TF+AS+SS-MoM3 Coordination-Based Molecular Assemblies as Electrochromic Materials: Ultra-High Switching Stability and Coloration Efficiencies**[1], ***Michal Lahav***, Weizmann Institute of Science, Israel

Layer-by-Layer (LbL) deposition, combined with metal-ligand coordination, has served as a powerful tool for generating functional architectures.[2] Such systems might find interesting applications in molecular electronics, sensor, solar cells and data storage. More significantly, owing to their interesting electrochromic (EC) behavior, they are promising candidates for use in smart windows and display devices. In this study we used a dip-coating process to generate molecular assemblies (**MA**) from metal polypyridyl complexes cross-linked with $PdCl_2$. These polypyridyl complexes are considered ideal chromophores for fabricating electrochromic materials, due to their excellent stability and light absorption that greatly depends on their oxidation state.[3],[4] The number of pyridine moieties of the chromophores is varied to control (i) the materials' stability, (ii) color, (iii) redox-chemistry, and (iv) the film growth (i.e., linear *vs.* exponential). We also observed that minor structural differences (i.e., the pyridine-bipyridine bond order) at the molecular level become apparent when the stability and electrochromic properties are examined (Figure 1). The **MA**s exhibit high coloration efficiencies and are extremely stable: they are thermally robust and have exceptionally high (spectro)electrochemical activity. Furthermore, we demonstrated the formation of a first-generation solid-state set-up.[1],[5]

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2) R. J. Mortimer, *Annu. Rev. Mater. Res.*, **2011**, 41, 241.

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4) G. de Ruiter, M. Lahav, H. Keisar, M. E. van der Boom, *Angew. Chem., Int. Ed.* **2013**, 52, 704-709.

5) M. E. van der Boom, M. Lahav, S. Shankar, US Patent 61/906,565, **2013**.

9:20am **TF+AS+SS-MoM4 New Approaches to the Preparation of Well-defined Metal Films on Top of Self-assembled Monolayers**, ***Michael Zharnikov***, Universität Heidelberg, Germany

Self-assembled monolayers (SAMs) can be potentially used as ultrathin insulating dielectric layers or intermediate films in different electronic and spintronic devices. Whereas the bottom electrode in such assemblies is represented by the metal substrate, the top electrode should be prepared at the SAM-ambience interface. Regretfully, the formation of a well-defined metal film on top of the SAMs is a non-trivial task, since the metal atoms deposited onto the SAM-ambient interface do not stay there, but penetrate into the monolayer and diffuse to the metal substrate following a strong thermodynamical drive. Here I discuss three new approaches to suppress the above penetration and diffusion, taken a representative ferromagnetic metal, nickel, as a test adsorbate. The first approach relies on irradiation-induced cross-linking of a thiol-substituted aromatic SAM. Whereas 2D-polymerization of such a SAM prevents penetration of the metal atoms into the monolayer, the thiol groups at the SAM-ambient interface serve as nucleation centers for the growing "top" film. The second approach, relying on SAMs of perfluoroterphenyl-substituted alkanethiols, utilizes a chemical reaction between the SAM constituents and adsorbate atoms. The primary process is the Ni mediated loss of fluorine atoms followed by extensive cross-linking between the partly defluorinated molecular backbones. The stability of these backbones and the rapid development of the cross-linking are the key components to hinder the metal penetration. Finally, the penetration of deposited metal atoms into a SAM can be nearly completely inhibited by the preliminary formation of palladium-chloride seeding layer at the SAM-ambience interface. The palladium atoms in the seeding layer serve as nucleation centers for the growing metal film, staying at its bottom during the growth. In contrast, the chlorine atoms are transferred from palladium to the deposited metal, staying on the top of the growing metal film and serving as surfactants.

9:40am **TF+AS+SS-MoM5 N-Heterocyclic Carbenes as Novel Ligands for Self Assembled Monolayers on Gold**, ***Cathleen Crudden***, Queen's University, Canada **INVITED**

The use of N-heterocyclic carbenes (NHCs) to modify homogeneous metal catalysts is widespread, however despite the versatility of these complexes, the high metal–NHC bond strength and oxidative stability of NHC–ligated metals, and the ease of synthesis of NHCs, there have been only a handful of reports of mostly ill-defined surfaces funtionalized by NHCs.

We will describe the the use of NHCs to form self-assembled monolayers on gold surfaces. In particular, films prepared by the deposition of 1,3-dihydro- 1,3-bisisopropylbenzimidazol-2-ylidene, show molecular ordering on the surface and remarkable stability. They show no decomposition upon heating for 24 hrs in THF, in boiling in water for 24hrs or upon treatment with acid (pH 2) or base (pH 12). Incredibly, they even survive largely after 24 hr exposure to hydrogen peroxide. This remarkable increase in stability relative to thiol-based SAMs will greatly increase the number of reagents and conditions to which the SAMs can be exposed.

The use of these films in SPR-based biosensing will be described, as will novel methods for the preparation of such films that can be carried out in air on the bench top.

10:40am **TF+AS+SS-MoM8 Improved Stability of Ag Thin Films due to Several Organic Surface Monolayers**, ***Midori Kawamura***, Kitami Institute of Technology, Japan*, C. Kudo, T. Sasaki, Y. Abe, K.H. Kim, T. Kiba*, Kitami Institute of Technology

Due to excellent physical properties, Ag thin films have been used as low-e coating, optical mirror, and so on. It is necessary to prevent degradation of the Ag films in air or humid atmosphere. For the purposes, it has been reported that several metal oxide nanolayers and organic monolayers are effective to make Ag thin films stable. Previously, we reported that modification of Ag films with 3-mercaptopropyltrimethoxysilane (MPTMS) monolayer can improve durability of the Ag films after environmental tests because strong bonds were formed between thiol moiety and Ag films, and also between silanol moiety and glass substrate. In the present study, we attempted to use other type of organic molecules, namely straight chain alkylthiols, such as 1-octadecanthiol (1-ODT), 1-dodecanthiol (1-DT) for protection of Ag film surface and compared with MPTMS.

Ag thin films (10nm) were deposited on clean glass substrates by vacuum evaporation. Then monolayer of 1-ODT and 1-DT were formed over the Ag thin films by solution method. The samples were kept in a constant temperature and humidity chamber (40 degree Celsius and 90 RH%) for a week. The electrical resistance, surface morphology, optical transmittance were measured before and after the test. Ag film without the monolayer, and that with MPTMS were also examined for comparison.

The surface roughness of the Ag film without the monolayer drastically increased from 2.7 nm to 27 nm after the test. However, the increase was within 1nm on Ag films with 1-DT and 1-ODT surface layers. These changes were smaller than that on Ag film with MPTMS surface layer. By the measurement of electrical resistivity, it was found that increase in the resistivity after the test was very much suppressed in the Ag film with these monolayers. In addition, optical transmittance measurement showed that transmittance spectrum of Ag films with these monolayers did not change after the test. These results accord with the Ag film morphology change. Consequently, excellent passivation effect of 1-DT and I-ODT surface monolayers on Ag films was confirmed.

11:00am **TF+AS+SS-MoM9 Electronic Structures of the Biaxially-strained GaSb(111) Films**, ***Takuya Hatayama***, The University of Electro-Communications (UEC-Tokyo), Japan*, A. Akaishi,* The University of Electro-Communications (UEC-Tokyo)*, J. Nakamura*, The University of Electro-Communications (UEC-Tokyo), Japan

III–V compound semiconductors have been extensively researched as alternative channel materials of complementary metal-oxide-semiconductor devices because of their superior carrier mobility[1]. In particular, GaSb is one of the promising p-channel materials, because its hole transport properties are significantly improved compared to Si. Recently, Ohtake *et al*. Have reported that high-quality GaSb films can be epitaxially grown on the Si(111) substrate using the InAs buffer layer[2]. The lattice constant in the plane of growth for the thin GaSb epilayer inherits the lattice constant of InAs, causing an inherent strain in the GaSb film. As a result, the electronic structure of the GaSb film can be modified. In this study, we evaluate the electronic properties of the strained GaSb bulk and the (111) films, especially the band gap formation, the effective mass, and the electronic conductivity, using first-principles calculations within the density functional theory. In general, the local density approximation (LDA) is commonly applied to the exchange correlation term. However, it has been well-known that the band gap of semiconductors is significantly underestimated with LDA. In order to rectify the underestimation of the band gap and to correctly evaluate electronic dispersions at band edges, we use the hybrid functional proposed by Heyd-Scuseria-Ernzerhof (HSE06) for the exchange-correlation term[3]. The spin-orbit interaction is also included.

We assume the biaxial strain parallel to the GaSb (111) plane. For the bulk with a direct band gap at ambient pressure, GaSb becomes an indirect band gap material under the compressive biaxial strain. The biaxial strain makes the twofold-degenerate heavy-hole and light-hole bands split into two bands at the Gamma point of the valence band. Interestingly, under the biaxial tensile strain, the effective mass of holes becomes anisotropic. We will also report on changes in electronic properties of the GaSb (111) ultrathin films under the biaxial strain.

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11:20am **TF+AS+SS-MoM10 How to Repel Polymer Adsorption on Flat Surfaces?**, ***Zhanhua Wang***, *S.P. Pujari, M.M.J. Smulders, H. Zuilhof*, Wageningen University, Netherlands

Organic monolayers or polymer brushes, often in combination with surface structuring, are widely used to prevent nonspecific adsorption of polymeric or biological material on sensor and microfluidic surfaces. Here we show for the first time how robust, covalently attached alkyne– derived monolayers or ATRP-produced polymer brushes, with a varying numbers of fluorine atoms, on atomically flat Si(111), effectively repel a wide range of apolar polymers without the need for micro– or nanostructuring of the surface. We have studied the antifouling property of fluoro-hydro monolayers and of fluorine-containing polymer brushes towards a range of commonly used polymers/plastics with comparable molecular weight in non– aqueous solvent, and have investigated the effect of polymer molecular weight on the fouling behavior. These studies relied on a range of characterization methods: wettability studies, ellipsometry, X– ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). We developed a novel surface morphology survey by AFM characterization that can accurately quantify the degree of fouling.

These studies consistently displayed that especially the mono–fluorinated (F1) monolayer shows excellent anti– fouling behavior, even more so than e.g. corresponding monolayers with perfluorinated alkyl tails. In this presentation the causes of this unprecedented and surprising finding are discussed. Second, we will focus on polymer brush properties that further reduce the adsorption of polymers. These findings and analysis offer significant potential for antifouling applications of ultrathin and covalently bound fluorine– containing coatings for a range of micro– and nanotechnological applications.

11:40am **TF+AS+SS-MoM11 Symmetric Attachment of Annulated Aromatic Hydrocarbons in Self-assembled Monolayers by Use of Oxazoles**, *C. Partes,* University of Frankfurt, Germany*, S. Schuster, T. Wächter,* University of Heidelberg, Germany*,* ***Martin Kind,*** University of Frankfurt, Germany*, M. Zharnikov,* University of Heidelberg, Germany*, A. Terfort*, University of Frankfurt, Germany

Self-assembled monolayers (SAMs) have proven to be powerful tools for tuning surface properties because of the uncomplicated method of their preparation and the high variability of their organic moieties. The suitability of SAMs in applications like, e.g., organic electronics is frequently investigated. An aim for the use of SAMs is the reduction of injection barriers that occur at the interfaces between organic semiconductors and technologically relevant substrates like gold or silicon.

A SAM ideal for this purpose should exhibit a high vertical conductivity. In view of this, we investigated several aromatic and araliphatic SAMs, e.g. terphenyl-terminated monolayers on gold [1]. In a more recent ansatz, we have examined SAMs bearing annulated moieties such as anthracene, which in contrast to oligophenyls are entirely planar [2]. However, as a consequence of the asymmetric substitution of anthracene to the thiol anchor group it is hardly possible to alter the tilt angle of these thiolate molecules within the SAMs [2].

To overcome this drawback, we extended the annulated system of the SAM-forming thiols with an oxazole unit, which allows for a quasi-symmetric attachment to the ancor group. This restores the possibility to influence the tilt angle of the aromatic units using the so-called odd-even effect in SAMs.

Here, we like to present preliminary results on preparation and structural properties of SAMs made from aromatic oxazole thiols on gold surfaces.

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Vacuum Technology
Room: 230B - Session VT-MoM

Vacuum Measurement, Calibration, and Primary Standards
Moderator: Bob Garcia, MKS Instruments, Joe Becker, Kurt J. Lesker Company

8:20am **VT-MoM1 History of Widely Used Vacuum Gauges and the Variations and Motivations That Occurred Along the Way: How Did We Get Where We Are?**, ***Paul Arnold***, MKS Instruments,Inc.,Granvillle-Phillips Product Center **INVITED**

A historical development of low vacuum, high vacuum and UHV gauging will be presented, covering the beginnings of capacitance diaphragm gauges, Pirani gauges including modernization in recent decades, triode gauges, Schulz-Phelps gauges, Bayard-Alpert hot cathode ionization gauges from their start to their modernization, various cold cathode discharge ionization gauges, and the spinning rotor gauge. The thread of design motivations that occurred over decades will be followed from not being able to measure the likely base pressures, to a drive for accuracy and stability over the full ranges of the gauges, to finally in recent decades, a priority for gauges to have lifetimes which better withstand the environments of processing chambers with aggressive gasses. The limitations of all these gauge technologies will be discussed. The history of methods for studying behavior of charged particles in electric fields before computer simulation, during its beginnings, and finally using the SIMION program, will be shown. Historical development of gauge calibration methods and standards will be presented, starting from mechanical methods, through bare-bones first principles methods, their evolution to more precise methods, and to finally some modern-day new physical standards for measuring pressure.

9:00am **VT-MoM3 MicroPirani MEMS Sensors for Vacuum Pressure Measurement - Looking Back and Ahead**, ***Caspar Christiansen***, *O. Wenzel*, MKS Granville-Phillips Division, Denmark

It has been almost two decades since the invention of the MicroPirani MEMS sensor and its first introduction to the realm of vacuum pressure measurement. Based on the principle of thermal conductivity the MicroPirani sensor is in many ways similar to the traditional Pirani sensor that has been used for many decades for vacuum pressure measurement. Though similar, the MicroPirani offers several advantages, when compared to the standard Pirani including: a wider measuring range (1*10^-5 torr to atmospheric pressure), better accuracy, better thermal stability, increased robustness and lifetime. Over the last few years our group has dedicated significant effort to the understanding of the interactions between the MicroPirani MEMS sensor and several process chemistries with the ultimate goal of improving accuracy and long-term stability. As an example of our most recent progress, a new coated version of the MicroPirani sensor will be presented to address potential issues relating to corrosive gases in some of the most demanding vacuum applications. The coating does not compromise the current performance of the MicroPirani but serves as a protective layer for all MEMS sensor components.

9:20am **VT-MoM4 Performance Assessment of Absolute Capacitance Manometers Used in Long-term Irradiation Studies**, ***Lily Wang***, *P.D. Honnell*, Los Alamos National Laboratory

Absolute capacitance manometers (MKS121A) are used in our experiments to measure gas release of materials resulted from long-term low-dose-rate radiation exposures. The experiments involve irradiating the samples in sealed metal vessels initially under vacuum (~10-6 torr). An absolute capacitance manometer is mounted on this sealed vessel to measure the pressure of gas being accumulated from the radiolytic decomposition of the material. Recently, a set of these long-term irradiation experiments was completed. The pressure gauges had been in continuous service for almost three years (987 days) in these experiments. Of the total service time, the gauges were exposed to the Cs-137 gamma radiation for 640 days. After decommissioning these samples, the gauges were checked with a recently calibrated pressure measurement station to assess their post-irradiation measurement performance. Additionally, two gauges that exhibited an unusual behavior of measuring decreasing pressure with time during the last ~350 days are being further tested for long-term stability with this active gas. This talk will present the results of the performance assessment and the long-term stability test and discuss the pressure measurement uncertainty in this type of experiments.

9:40am **VT-MoM5 Analysis of Pressure Measurement Techniques from 1 kPa to 130 kPa**, ***Jacob Ricker***, *J. Hendricks*, National Institute of Standards and Technology

The most frequently measured pressures are those in the barometric regime. These measurements are used for everything from altimetry to weather and significant resources have been spent in the past couple years improving barometric measurements. Recent improvements in devices covering this range have drastically reduced their uncertainties, making 0.01% or lower very common. However for vacuum measurement (100 kPa > P > 0.01 Pa), most often people use the capacitance diaphragm gauges (CDG) for their resolution and ability to reach the lower pressures. The capacitance gauges are very prone to drift making uncertainty of 0.25% an average expectation for performance for a high end device. However, by pairing a capacitance gauge to a barometric sensor to compare the values at 1 kPa, a CDG can be corrected to reduce the uncertainty to as low as 0.05%. This technique will be incorporated into the NIST Portable Vacuum Standard (PVS) reference instrument that can be provided for calibration of vacuum gauges at a customer's facility.

Key to this concept is the accuracy and uncertainty of the barometric sensor. NIST has been evaluating measurement methods by taking different high accuracy barometric gauges into the vacuum regime. We have shown that less than 0.05% is easily achievable at 1 kPa and might be even be achievable at 0.1 kPa. The results will be presented for different gauge types, measurement methods, and manufacturers. The talk will include discussions on accuracy, noise, and stability and an uncertainty estimation of using this technique.

10:00am **VT-MoM6 Comparisons between Capacitance Diaphragm Gauges with Different Types of Diaphragm Materials using Force-balanced Piston Gauge**, ***HanWook Song***, KRISS, Korea, Republic of Korea, *M. Salazar*, UST, Republic of Korea, *S.Y. Woo*, KRISS, Korea, Republic of Korea

Capacitance Diaphragm Gauge (CDG) has been one of the most accurate check or transfer standard ranging from low pressure to the high vacuum region. Nowadays, it would be practical to cover wide range of measurement in the least number of equipment possible. Knowledge on the equipment, in this case, transducer's performance establishes not only its use but the accuracies it can maintain. CDG's accuracies depend mostly on linearity, hysteresis and repeatability. In this paper, six (6) commercially available CDGs of two different diaphragm types, one with metal and the other with ceramic, were performance checked through comparison to a reference standard, a Force-balanced Piston Gauge (FPG), through repeated measurements ranging from 0.01 Torr to 100 Torr at different times over a month period. Performance of CDGs were observed at 10% of its full capacity to characterize its feasibility to measure at its lowest range (vacuum region), thus, its practicability to cover wide range of pressure measurement. Results showed that the maximum deviation from the standard of the CDGs with metal diaphragm is 2.24% and 1.52% and the CDGs with ceramic diaphragms 8.37% and 1.39% at low and high range respectively. Additionally, CDGs with metal diaphragm showed similar pattern of accuracy changes with pressure on both the low and high range. On the other hand, the CDGs with ceramic diaphragm showed conflicting pattern of accuracy changes with pressure on different ranges. In conclusion, no matter how the CDGs are behaving on certain ranges, these results can establish the accuracies of the CDGs tested and may further be supported by repeating same tests at a later time.

10:40am **VT-MoM8 Inverted Magnetron with Different Cathode Materials**, ***Martin Wüest***, *J. Marki*, INFICON Ltd., Liechtenstein

We have recently developed an inverted magnetron with an exchangeable ionization chamber. The standard version has cathode walls made of stainless steel. We investigated ionization chambers that are made of different cathode materials such as Ni or Ti. For these materials, differences in a long-term self-sputtering test in Ar gas as well as in the anode current vs pressure characteristic were found.

11:00am **VT-MoM9 Modern Day Challenges to Ionization Gauge Lifetimes**, ***Gerardo Alejandro Brucker***, *S.C. Heinbuch, T.R. Swinney*, MKS Granville-Phillips Division, Longmont

Ionization gauges were introduced into the vacuum market over half a century ago with the initial intent of extending pressure measurement ranges into the ultrahigh vacuum range. In more recent years, ionization gauges have been pushed into industrial applications with total pressures as high as 100 mTorr while operating in the presence of both reactive and corrosive gases. The harsh chemical and physical environments of industrial process chambers present very serious challenges to the lifetime of modern ionization gauges. Lifetime is defined as the time until the pressure gauge fails to either operate or produce measurements within its specified accuracy. Following the recent development of a new commercial cold cathode ionization gauge specifically designed to provide extended lifetime, our laboratory has been involved in root-cause analysis studies to understand gauge failures caused by the harshest process conditions. Our long term goal is to create a comprehensive knowledge-base of physicochemical interactions between processes and ionization gauges, provide best known vacuum measurement practices to the industry and develop longer lasting products that meet the demands of the modern vacuum market. In this presentation, we discuss a case study for a cold cathode gauge used in an ion implantation process that revealed some interesting and unexpected results. Most cold cathode gauge failure mechanisms reported in the vacuum technology literature have focused on sensitivity losses due to internal sputtering; however, we will illustrate an example in which a different phenomenon eventually led to gauge failure. It is evident to our group that discovery is far from over and that gauge lifetime challenges are continuously evolving.

11:40am **VT-MoM11 Photonic Realization of the Pascal: The Future of Pressure and Vacuum Metrology?**, ***Jay Hendricks***, *J.E. Ricker, A. Stone, F. Egan, E. Scace, F. Strouse*, National Institute of Standards and Technology

NIST is actively developing a new paradigm in the methodology of pressure and vacuum gauging and metrology. In a break with nearly 400 years of mercury based primary standards, we are now poised to develop a new standard that is based on the fundamental physics of light interacting with a gas. For the vacuum community, this represents a shift in how we think about the unit of the Pascal in that it will be directly related to the density of a gas, the temperature, the refractive index, and the Boltzmann constant. The photonic technique has now achieved important benchmarks in performance when compared to the existing primary standards based on mercury manometers: The photonic technique has a 20X smaller footprint, 100X faster sensing response time, 100X lower pressure range, and for an emerging technique has demonstrated impressive accuracy, reproducibility and hysteresis. Photonic sensing of the pascal has the potential to be further miniaturized, and has the key advantage that the light used for sensing the pressure can be transmitted over light-weight, high-speed fiber optic cables and networks.

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.

Atom Probe Tomography Focus Topic
Room: 230A - Session AP+AS-MoA

Current and New Research Fields for Applications of Atom Probe Tomography
Moderator: Baishakhi Mazumder, Center for Nanophase and Materials Sciences Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

2:20pm **AP+AS-MoA1 APT Studies of the Embrittlement of Fe-Cr Ferrite**, ***Mattias Thuvander***, Chalmers University of Technology, Sweden, *J. Odqvist, P. Hedström*, KTH Royal Institute of Technology, Sweden **INVITED**

Ferrite containing more than a few percent chromium is susceptible to embrittlement when subjected to elevated temperatures for sufficiently long periods of time. The phenomenon is often called '475°C embrittlement', indicating the temperature at which the effect is most rapid. The embrittlement is an issue for several important types of steel, including corrosion resistant ferritic steel, duplex stainless steel, cast austenitic steel and austenitic weldments, and limits their maximum service temperature (to about 300°C). The volume fraction of ferrite ranges from 100% in ferritic steel, to about 50% in duplex steel, down to 5-25% in austenitic castings and weldments (for which the presence of some ferrite is needed to avoid solidification cracking). The reason behind the embrittlement is the phase separation into two bcc-phases, Cr-rich α' and Fe-rich α, as can be seen in the binary Fe-Cr phase diagram. The phase separation results in an increase in strength and hardness but a decrease in ductility. Depending on Cr-content and temperature, the phase separation occurs by nucleation and growth (typically for low Cr contents) or by spinodal decomposition (typically for high Cr contents). Spinodal decomposition is an interesting phenomenon in physical metallurgy and it has been extensively studied for a long time. The phase separation occurs on the nanometer scale and during the early stages the concentration variations are subtle. Therefore, it is a challenging mechanism to study experimentally. Atom probe tomography (APT) is a well-suited technique, as small concentration variations on a small scale can be measured, also in the case when the phase separation has a complex 3D-structure, which is the case for spinodal decomposition. In this presentation, APT methodology for studying spinodal decomposition will be discussed. Also, results from several investigations concerning phase separation kinetics will be presented. For example, the influence of stress on spinodal decomposition in duplex steels, the influence of homogenization temperature on spinodal decomposition in binary Fe-Cr and the behavior of different ternary Fe-Cr-X systems will be addressed.

3:00pm **AP+AS-MoA3 Comparing APT Mass Spectral Ranging for Compositional Accuracy: A Case Study with Cast Duplex Stainless Steels**, ***Daniel Perea***, *A. Eaton, J. Liu,* Pacific Northwest National Laboratory, *S. Mburu, S. Schwarm, R. Kolli, S. Ankem*, University of Maryland

The mass spectrum of an atom probe tomographic analysis is a superposition of correlated mass-to-charge-state peaks and uncorrelated background counts. The compositional accuracy of a volume of material measured via atom probe tomographic analysis is dependent upon the manner in which the individual mass spectral peaks are ranged for integration. However, an accurate calculation of composition can be challenging due to a combination of complicated peak shapes, peak overlap, and background counts. Using data from both the *α*–ferrite and *γ*–austenite phases of a cast duplex stainless steel , we illustrate a methodology to account for the background counts, as well as to deconvolute overlapping peaks, in order to calculate composition that we compare to energy dispersive x-ray spectroscopy measurements.

3:20pm **AP+AS-MoA4 Chemical Imaging of Atmospheric Aerosols using Atom Probe Tomography and Multi-Modal Characterization**, ***Jia Liu***, *M.I. Nandasiri, L. Gordon, G. Kulkarni, V. Shutthanandan,* Pacific Northwest National Laboratory, *S.A. Thevuthasan,* Qatar Environment and Energy Research Institute, Qatar, *A. Devaraj*, Pacific Northwest National Laboratory

Global climate is significantly dictated by small particulates in the atmosphere known as aerosols. These atmospheric aerosol particles when subjected to certain humidity and temperature conditions can induce heterogeneous ice nucleation, which is directly sensitive to aerosol surface structure and chemistry. These ice nuclei are the precursors to snow fall and precipitation. Often natural atmospheric aerosols are found to be coated with sulfates and organic molecules. Elucidating the mechanism responsible for ice nucleation on coated or bare atmospheric aerosols requires understanding the structure, composition and chemical state of coated and bare aerosols. At EMSL we are developing a multimodal approach for imaging bare and coated aerosols utilizing a combination of atom probe tomography (APT), imaging X-ray photoelectron spectroscopy (XPS), focused ion beam scanning electron microscopy (FIB-SEM) and transmission electron microscopy (TEM). Imaging XPS provides the composition and chemical state of organic or inorganic elements within the top 5nm of the surface of aerosol particles with a spatial resolution of ~3 µm. FIB-SEM aids in understanding the morphology and porosity of particles both on the surface and sub-surface. TEM provides the atomic scale structural information and laser assisted APT provides sub-nanoscale compositional mapping of aerosols. TEM and APT are sub-single particle analysis techniques and can complement the individual aerosol particle measurements provided by the single particle laser ablation time of flight mass spectrometry (SPLAT). All these techniques provide specific multiscale chemical and structural information about the aerosol particles from the macro- to the atomic-scale. Specific examples from multimodal chemical imaging of mineral dust aerosols coated with varying concentration of sulfuric acid or organics will be presented along with the direct insights gained through this approach for improving ice nucleation parameterizations.

3:40pm **AP+AS-MoA5 Combining Atom Probe Tomography with TKD and FiB for Comprehensive Characterization of High Performance Materials**, ***Sophie Primig***, University of New South Wales, Australia, *K. Babinsky, P. Haslberger, C. Hofer, D. Lang, C. Turk*, Montanuniversität Leoben, Austria **INVITED**

Despite the increasing interest in atom probe tomography, this technique has so far almost exclusively been applied for chemical analyses of materials at the atomic scale. As nowadays the frontiers of material science are more and more being pushed towards the nanostructure, advanced comprehensive characterization techniques which provide both chemical and crystallographic information are required. For the crystallographic analysis of atom probe specimens several complementary techniques such as transmission electron microscopy have been applied that all have their advantages and drawbacks. Different approaches try to establish crystallographic information directly from the atom probe data itself which is still computationally challenging and not always possible. Another recently proposed straightforward way of quickly obtaining crystallographic information is the application of transmission Kikuchi diffraction on atom probe tips prior to the atom probe experiment. This procedure has so far only been successfully applied for positioning of grain boundaries close to the apex of the tips via focused ion beam milling.

The aim of the current study is to show applications of transmission Kikuchi diffraction on atom probe specimens of high performance materials and to demonstrate the strengths as well as the limits of these two complementary techniques. Four examples are shown which include boron segregation at prior austenite grain boundaries in a heat treatable steel, interlath retained austenite films with cementite in a bainitic steel, molybdenum carbides in a molybdenum alloy, and the preparation of grains with well-defined crystal directions in the tip axis of an iron-cobalt-molybdenum alloy.

4:20pm **AP+AS-MoA7 Atom Probe Tomography Studies of FeCo Nanocomposite Soft Magnetic Materials**, *A. Leary, V. Degeorge, V. Keylin,* Carnegie Mellon University, ***Arun Devaraj***, *J. Cui,* Pacific Northwest National Laboratory, *M. Mchenry*, Carnegie Mellon University

Nanocomposite soft magnetic materials exhibit high magnetization and low coercivity for application in power electronics, motors, and sensors. The composite nature of these materials, created by thermal annealing of rapidly solidified metallic glasses, offers many options to tune desired material properties. Grain sizes below ~30 nm are relevant to average the magnetocrystalline anisotropy between neighboring grains within an exchange volume. Chemical partitioning during devitrification creates variations in local composition compared to the nominal alloy composition. These variations impact material properties such as magnetostriction, Curie temperature, and grain size. Local composition measurements of annealed nanocomposites by Atom Probe Tomography link observed magnetic properties to the material structure. The impacts of chemical partitioning on diffusion limited grain growth, intergranular coupling at high temperature, and induced anisotropy are discussed.

Applied Surface Science
Room: 212D - Session AS-MoA

Practical Surface Analysis I: Interpretation Challenges
Moderator: Karen Gaskell, University of Maryland, College Park, Alan Spool, HGST, a Western Digital Company

2:20pm **AS-MoA1 ASSD 30th Anniversary Lecture: XPS: Three Challenges and an Opportunity**, ***James Castle***, University of Surrey, UK **INVITED**

The 3 challenges refer to ambitions that have been on the books for many years.:

1, to obtain XPS data from individual sub-micro particles using a laboratory instrument. Cazaux (1975) scanned an electron beam across the reverse of an Al foil holding the particles. A similar arrangement was adopted by Jenkins and Castle (1994), Their object was to examine the interface region of microtomed thin sections of adhesive joints. Useful parameters were determined but this, reverse-side excitation of x-rays is not easily adapted for use in a laboratory instrument. Recently Castle et al(2013) have returned to the subject using an Auger spectrometer. The particles are scattered on Al or Mg foil from which X-rays are produced by the impact of an electron beam close to the particle. Examples will be given

2, the need to make the Auger Parameter (AP) more intuitive. The AP, Wagner (1974), depends on the relaxation energy of the chemical structure. It is so easily determined but yields a number that is so readily forgettable! Mg has a value of 2488eV whilst Ca is 644eV. West and Castle(1982) showed how a universal scale for the AP might be produced. The zero point is that for a non-polarisable lattice. Since the refractive index (RI) also depends on lattice polarizability the zero-point can be found using the value of RI = 1 on a suitable plot and thus elements placed on a common scale. More recently (2002), Castle et al used the method to compare AP'S for V and O for a series of compounds It is concluded that a universal scale would greatly benefit those in applied surface chemical analysis .

3,is codifying the procedures that would enable manufacturers to give a first estimate of near-surface structure from the survey scan: helping to plan the detail scans which follow the survey. Castle and Baker (1999) gave an indication of how this might be approached and a very detailed set of rules was published by Castle (2007) An ISO standard for recognition of a C1s peak as contamination is being developed by ISO TC201. With this, manufacturers should have the confidence that any automated data processing will have the backing of users.

The **opportunity** would bring to fruition the vision of those members of ASSD when they launched Surface Science Spectra as a Journal and a database in 1993. As a Journal it is still unique in our field and is much valued for its provision of reference spectra for materials of current interest. The opportunity is to provide a searchable data base of peak energies for all elements in the diverse set of 1000 materials included in the 22 volumes now available.

3:00pm **AS-MoA3 Results from a VAMAS Inter-Laboratory Comparison on the Measurement of Composition of Organic Mixtures in Depth Profiling**, ***Alexander Shard***, National Physical Laboratory, UK

Argon cluster sources for 3D analysis of organic materials are starting to become routinely used in material analysis. Most new XPS and SIMS instruments are now equipped with such sources and are finding widespread use in both academia and industry. The purpose of a depth profile is to measure the distribution of chemical species and therefore it is important to assess the ability of various techniques and approaches to provide this information. One of the most popular analytical methods to combine with cluster beam sputtering is SIMS. This method provides excellent specificity, high sensitivity in most cases and enables discrimination of compounds that cannot be matched by other methods such as XPS. However, there are a number of factors that prevent organic SIMS from being quantitative. For XPS there is a well-established route to obtain chemical compositions, which is its primary advantage in organic depth profiling.

Until recently, organic SIMS data could be used to identify compounds, and could only measure concentrations in special cases. The major limiting factor in SIMS is the 'matrix effect' which has not been the subject of any substantive or coordinated investigation since the genesis of organic SIMS analysis in the 1980s. Fortunately, the ability provided by argon cluster sources to perform nearly damage-free profiles of organic materials allows us to begin to address this effect.

Mixed molecular materials of known composition have been made with sufficient precision and stability for a reliable analysis to be performed. The materials demonstrate, unambiguously, that matrix effects are significant in molecular SIMS experiments, but also that these effects can be measured and described. It is found that the matrix effects are remarkably consistent between laboratories and appear to depend upon two main factors: the identity of the secondary ion and; the analytical source used. Furthermore, it is possible to establish normalization schemes that compensate for the matrix effect whilst also eliminating the other major source of error in quantitative SIMS: instability and drift in the primary beam current.

This talk will describe VAMAS project A3(g), the SIMS matrix effect and implications in the quantitative analysis of SIMS depth profiles. These effects are not restricted to compositional analysis but also have a profound influence on the apparent position of interfaces, often contributing the major source of uncertainty to the measurement of the thickness of an organic layer.

3:20pm **AS-MoA4 *In Operando* Studies of High Temperature, Heterogeneous Electrocatalysis on a Lanthanum Strontium Manganite-based Solid Oxide Electrochemical Cell**, ***Aaron Geller***, *B. Eichhorn*, University of Maryland, College Park

Near ambient X-ray photoelectron spectroscopy (APXPS) was used for *In Operando* studies on lanthanum strontium manganite (LSM, $La_{0.8}Sr_{0.2}MnO_{3\pm\partial}$) electrodes, one of the most popular materials currently in use on solid oxide electrochemical cells (SOCs). SOCs consisting of two LSM electrodes on a yttria-stabilized zirconia (YSZ) electrolyte were probed in an oxygen atmosphere (0.5 Torr) at ~600 ºC under open circuit voltage (OCV) and polarized conditions. Polarization promotes the oxygen reduction reaction (ORR, cathodic reaction) on one LSM electrode and oxygen evolution reaction (OER, anodic reaction) on the other. Through use of an area detector, electrochemically-induced phenomena on the surface of the cell such as surface potential mapping, Sr segregation, and changes in the Mn oxidation state were observed and spatially resolved to within 20 microns.

By tracking shifts in the La 4d and Sr 3d peaks under polarization relative to OCV, local surface potentials of each LSM electrode were determined and it was observed that the majority of electrochemical activity, signified by a sharp potential drop, was located at the LSM/YSZ interface (shifts in the Zr 3d peaks were used to determine the local potential of YSZ). Several challenges in interpretation were found, the most surprising of which was a potential separation between the lanthanum and strontium components of the LSM lattice which were expected to exhibit the same potential under bias. Instead, the lattice La was driven to a higher potential than the lattice Sr on both electrodes. Furthermore, it was found that lattice Sr was relatively depleted under bias on each electrode, though the effect was more pronounced on the OER side. Sr 3d spectra also showed two different species under bias, lattice Sr and surface-segregated SrO, with the surface species shifted to a higher potential than the lattice Sr species. The data analysis process of these complex systems presented several challenges as well, which will be discussed.

3:40pm **AS-MoA5 Building the Link Between XPS Data and Functional Properties of Materials**, ***Kateryna Artyushkova***, *I. Matanovic, S. Kabir,* University of New Mexico, *B. Kieffer,* New Mexico State University, *A. Serov, P. Atanassov*, University of New Mexico **INVITED**

Building structure-to-property relationships is one of the most often attempted research tasks in today's chemistry of materials. Often relationships are directly dependent and easy to identify. In complex, nano-structured functional materials, those correlations are intertwined and multi-directional. Predicting macroscopic property of interest, such as activity, wettability, stability, etc., based on correlation with materials surface chemistry is challenging but yet accomplishable.

The relationship between functional property and the chemical structure of materials is typically established through correlations between performance metrics parameters and various spectroscopic techniques, including XPS, XANES, XPES, TOF-SIMS, and Mössbauer spectroscopy. The primary advantage of XPS in the characterization of heterogeneous multicomponent nanostructures is the ability to discriminate between different surface oxidation states and chemical environments. However, the assignment of XPS peaks in highly heterogeneous materials is not straightforward. A significant improvement in the assignment of peaks at various binding energies could be achieved using reference materials, yet, many relevant reference materials do not exist. State-of-the-art computations allow the determination of BE shifts for specific defect chemistries and geometries, providing valuable information for processing and interpretation of spectra data.

In this talk, I will discuss approaches towards structure-to-property relationships derived for energy-related materials, such as electrocatalysts for fuel cell and biocatalysts for microbial fuel cells. I will discuss multivariate approaches towards correlating XPS data with performance characteristics and binding energy shift calculations using DFT for interpreting XPS spectra. Application of XPS instrumentation with in-situ capabilities to study materials under conditions relevant to their application will be also discussed.

4:20pm **AS-MoA7 Multitechnique Characterization of Protein G B1 Orientation on Surfaces**, ***Elisa Harrison***, *G. Interlandi, D.G. Castner*, University of Washington

The orientation of adsorbed proteins on surfaces has been shown to influence biological responses, so research and development of biotechnological applications (e.g., sandwich ELISAs) have focused on controlling the orientation of each protein layer. However, characterizing protein orientation has been a challenge. The goal of this research is to address these challenges by developing methodology to study multilayer protein systems. Specifically, we aim to determine the orientation of protein G B1, an IgG antibody-binding domain of protein G, on various surfaces and the effect of its orientation on antibody binding using a variety of surface-sensitive tools and simulations. We propose that binding selectivity will increase for well-ordered protein films due to high availability of binding domains. To achieve control over surface properties, we have utilized four types of self-assembled monolayers (SAMs) to control protein orientation: N-Hydroxysuccinimide-terminated SAMs and dodecanethiol SAMs to immobilize protein G B1 in a random orientation and maleimide-terminated SAMs and bare gold to immobilize cysteine mutants of protein G B1 in a well-ordered orientation. Developing methods using surface-sensitive, label-free tools, such as XPS, ToF-SIMS, and quartz crystal microbalance with dissipation monitoring, provide detailed information of the adsorbed proteins, such as composition, coverage, and orientation. Additionally, computational methods to predict the orientation of proteins on surfaces can help to interpret and complement experimental techniques. In this work, we describe the development of a simulator to determine protein orientation on a surface using Monte Carlo (MC) simulations. We chose two proteins to test the MC simulator: LKα14 peptide and protein G B1. We chose LKα14, a 14-mer consisting of only leucine and lysine amino acid residues, as a benchmark because of its predictable structure and orientation on hydrophobic surfaces. To test the MC simulator on a more complex system, we used protein G B1. Preliminary MC simulations show that protein G B1 is likely to interact with a graphene surface through residues Met1, Val21, Ala48, and the hydrophobic part of Lys10 on terminal ends of the protein. We will extend the MC algorithm to predict the orientation of additional protein/surface combinations and validate using experimental results. While the systems explored thus far are model systems that are far less complex compared to biological systems of the real world, we aim to develop methodology using state-of-the-art tools that can be continuously improved to help expand our knowledge of, and possibly control, biomolecules on surfaces.

4:40pm **AS-MoA8 Investigation of Composition and Structure of Functionalized Carbon Materials**, ***Svitlana Pylypenko***, *K.N. Wood,* Colorado School of Mines*, A.A. Dameron,* National Renewable Energy Laboratory*, R. O'Hayre*, Colorado School of Mines

While significant efforts has been placed on understanding the role of nitrogen in real, application based environments utilizing high surface area carbon supports, a lack of knowledge exists in understanding the specific functionalities and their role in improving performance. In this work we expand the understanding of nitrogen functionalized high surface area carbon supports by focusing on the careful analysis of the distribution of nitrogen functionalities through XPS and other complementary techniques, such as Raman and NEXAF spectroscopies. Functionalization of several high-surface carbons was performed using nitrogen ion implantation using a variety of ion implantation parameters. The results contained herein show that increasing implantation time only marginally elevates nitrogen concentration, forming mostly single defect structures. Increasing the beam current results in formation of more complex defect structures containing clustered multi-nitrogen defects, similar to those observed in carbon nitride materials. We also show that higher nitrogen dosage levels create a more homogeneous distribution of nitrogen functionalities, regardless of initial carbon material or the resulting nitrogen concentration.

5:00pm **AS-MoA9 How to Make Amorphous Carbon Stable: An *In Situ* XPS and NEXAFS Investigation of Thermally-Induced Structural Evolution of Amorphous Carbon Surfaces**, ***Filippo Mangolini***, Ecole Centrale de Lyon - LTDS, France*, J. Hilbert, J.B. McClimon, J.R. Lukes, R.W. Carpick*, University of Pennsylvania

Silicon oxide-doped hydrogenated amorphous carbon (a-C:H:Si:O) coatings are fully amorphous thin-film materials consisting of two interpenetrating networks, one being a hydrogenated amorphous carbon (a-C:H) network and the other a silica glass network. At temperatures above 150°C, pure a-C:H films undergo a rapid degradation that starts with the evolution of hydrogen and is followed by the conversion of sp^3 bonds to sp^2 [1]. However, a-C:H:Si:O exhibits much lower susceptibility to oxidative degradation, and higher thermal stability compared to a-C:H. This makes a-C:H:Si:O attractive for many applications, including next generation hard disk drives, which require overcoat materials that are thermally stable up to temperatures above 500ºC. Although it is well-established that a-C:H:Si:O possesses superior thermal stability and oxidation resistance relative to a-C:H, the scientific basis for this behavior is not understood. To investigate this, a combined *in situ* X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy study was performed. Changes in the surface chemistry and bonding configuration of a-C:H:Si:O (*e.g.*, silicon oxidation state, carbon hybridization state) were accessed *in situ* at temperatures up to 450ºC. A novel methodology for processing NEXAFS spectra, which makes it possible to account for the presence of a carbonaceous contamination layer on an air-exposed material, was developed [2]. This allowed quantitative evaluation of the carbon hybridization state in the film as a function of the annealing temperature. Upon high vacuum annealing, two thermally-activated processes could be determined to take place in a-C:H:Si:O by assuming a Gaussian distribution of activation energies with mean value E and standard deviation σ: a) ordering and clustering of sp^2 carbon ($E\pm\sigma$= 0.22±0.08 eV); and b) conversion of sp^3- to sp^2-bonded carbon ($E\pm\sigma$= 2.7±1.0 eV). The experimental results are in qualitative agreement with the outcomes of molecular dynamics simulations performed using the ReaxFF potential. To determine the environmental dependence of the surface structural evolution of a-C:H:Si:O, the results of the *in situ* XPS/NEXAFS investigation were compared to those for a-C:H:Si:O samples heated in air, showing a strong effect of atmospheric oxygen. These results provide guidance for designing modified materials able to meet ever-increasing performance requirements of coatings for demanding applications.

1. F. Mangolini, F. Rose, J. Hilbert, R.W. Carpick, Applied Physics Letters, 103, 161605, 2013

2. F. Mangolini, J.B. McClimon, F. Rose, R.W. Carpick, Analytical Chemistry, 86, 12258, 2014

5:20pm **AS-MoA10 A Comparative Study of the Native Oxide on 316L Stainless Steel by XPS and ToF-SIMS**, ***Sabrina Tardio***, *M.-L. Abel,* University of Surrey, UK*, R.H. Carr,* Huntsman PU*, J.E. Castle, J.F. Watts*, University of Surrey, UK

AISI 316L is an austenitic stainless steel which is widely used in applications that require a degree of resistance to crevice and/or pitting corrosion. The L identifier of 316L indicates lower carbon content than the standard 316 grade, a characteristic which reduces the susceptibility to sensitization (grain boundary carbide precipitation) and for this reason it is widely used in heavy gauge welded components. The corrosion resistance of stainless steel is a result of the presence of a thin oxide layer on its surface. The passivation of stainless steel takes place in atmospheric conditions which yields a film that is self-healing on localised damage. The oxide, naturally formed in the atmosphere, is generally referred to as the native oxide and it is affected by environmental factors and, for that reason, different methods are often employed to modify the oxide layer to make it suitable for particular applications. This steel is also widely used as a substrate for adhesion; it is one of the “technological surfaces” on which organic coatings are applied. In this context, differences in the chemistry of the surface, as a consequence of different treatments, will influence the degree and modality of interaction of the adhesives with this metal. Many works have studied stainless steel with the aim of understanding more about the modification of this oxide layer, but few have addressed the composition of the passive film in its air-formed or water exposed state. In this work, attention is focused on the composition of the native oxide and changes in its chemistry brought about by water exposure. The native oxide film on stainless steel is very thin, of the order of 2 nm, and known to be readily modified by immersion in aqueous media. In this paper, XPS and ToF-SIMS are employed to investigate the nature of the film in the air-formed and water emmersed states. The film is described in terms of oxide, hydroxide and water content. The preferential dissolution of iron is shown to occur on immersion. It is shown that a water absorbed layer and a hydroxide layer are present above the oxide-like passive film. The concentrations of water and hydroxide appear to be higher in the case of exposure to water. A secure method for the peak fitting of Fe2p and Cr2p XPS spectra of such films on their metallic substrates is described. The importance of XPS survey spectra is underlined and the feasibility of C_{60}^+ SIMS depth profiling of a thin oxide layer is shown.

Biomaterial Interfaces
Room: 211D - Session BI+AS-MoA

Characterization of Biological and Biomaterials Surfaces (2)
Moderator: Joe Baio, Oregon State University, Dan Graham, University of Washington

2:20pm **BI+AS-MoA1 Characterization of Protein G B1 Immobilized Gold Nanoparticles using Time of Flight Secondary Ion Mass Spectrometry and X-ray Photoelectron Spectroscopy**, ***Yung-Chen Wang****, *D.G. Castner*, University of Washington

Nanoparticles (NPs) have been widely used in many fields of science due to their unique physical properties. While many applications of NPs such as imaging probes or drug carriers often require the conjugation of proteins or biomolecules, the surface interactions between NPs and biomolecules remains underexplored. For example, the immobilization of immunoglobulin G (IgG) onto NP surfaces is critical for the development of many immunosensors and drug delivery nanocarriers. Notably, the orientation of the immobilized IgG can have a significant impact on clinical outcomes of nanocarriers by impacting its biostability and efficacy. One approach to control the proper orientation of IgG is by utilizing the IgG Fc tail binding proteins.

In this work, Protein G B1, a protein that will selectively bind to the Fc tail of IgG, was immobilized onto gold NPs (AuNPs) functionalized with maleimide and oligo-(ethylene glycol)(OEG) self-assembled monolayers (SAMs). Protein G B1 was immobilized on AuNPs using either carbonyldiimidazole (CDI) chemistry or maleimide-cysteine interaction. We use the surface sensitive analysis techniques of x-ray photoelectron spectroscopy (XPS) and time of flight-secondary ion mass spectrometry (ToF-SIMS) to characterize the immobilization of protein G B1. Unlike conventional NP characterization techniques such as dynamic light scattering (DLS) and UV/Vis, XPS and ToF-SIMS can provide additional information on the surface elemental composition, protein coverage and orientation.

XPS analysis confirmed the CDI activation of the OEG-SAMs AuNPs by detecting the nitrogen containing active intermediate and the attenuation of gold signal. After incubation with protein, the immobilization of the protein was demonstrated by the increased nitrogen signal on the surface. ToF-SIMS analysis also confirmed the successful functionalization, CDI activation, and protein immobilization by identifying signature secondary ions from each step of the protein immobilization process.

By comparing the ratio of secondary ion intensity originating from opposite ends of the protein, it was possible to determine the orientation of immobilized protein G B1. As expected, the non-site specific CDI chemistry did not lead to a specific protein orientation on the AuNPs. In contrast to CDI chemistry, we expect to control the orientation of the immobilized protein using maleimide functionalized AuNPs and cysteine mutants of Protein G B1 through site-specific carbon-sulfur interaction.

Overall, the systematic characterizations in this study will provide detail information of protein-NP interactions and serve as a platform for controlling the orientation of IgG on AuNPs.

2:40pm **BI+AS-MoA2 Controlled Molecular Mechanisms of Engineered Solid Binding Proteins on Surfaces**, ***Christopher So***, National Research Council postdoc cited at Naval Research Laboratory, *S. Walper,* US Naval Research Laboratory, *R. Stine,* Nova Research, *D.E. Barlow, K. Wahl*, US Naval Research Laboratory

Persistent and uncontrolled aggregation of proteins at surfaces remains a major challenge for biocompatibility, fouling, and biosensing. To fully realize the rich properties of proteins at interfaces, a critical link between displayed protein sequence and surface assembly mechanisms is required. Here we use rational protein mutations combined with *in situ* microscopy and spectroscopy methods to demonstrate that manipulation of solid binding and intermolecular interactions by proteins can dictate their surface behavior and induce nanostructure formation. We use streptavidin (SA) as a robust scaffold to control the density and localization of aromatic residues, expected to interact with surfaces such as graphite and graphene through pi-bonding. The surface adapted SAs are generated by placing aromatic side chains of varying polarity (Phenylalanine, Tyrosine, Tryptophan) along three putative permissive sites in a coplanar arrangement. The effects of these mutations on bulk solution structure, surface-associated structure, as well as surface affinity, orientation and spatial organization are studied *in situ* using attenuated total reflectance (ATR) infrared spectroscopy (IR) with linear polarization (LP), fluid-mode atomic force microscopy (AFM), and circular dichroism (CD). We have found that our simple modifications to mSA have little effect on the solution state of the protein, while having a pronounced effect on affinity and secondary structure in the adsorbed state. Through fabricating graphene-coated ATR-IR prisms, we find that unmodified mSA exhibits an ordered beta sheet structure at surfaces, while tryptophan modifications to mSA (Trp-mSA) induces a more disordered structure. We quantify by temporal ATR-IR spectra a *ca.* 4.5x enhancement in sticking probability for Trp-mSA over mSA to graphene. Fluid-mode AFM studies on graphite support a surface-mediated coarsening mechanism: while mSA forms no obvious surface structures, Trp-mSA aggregates and forms islands 10-50 nm in size over the course of an hour. Such disordered SA aggregates provide high affinity sites for slow lateral island growth processes, giving rise to a bi-modal exponential adsorption curve for Trp-mSA but absent in mSA. Ultimately, defining the molecular basis of protein self-assembly and the impact of displayed chemistries at liquid-solid interfaces will enable rationally designed biological surface coatings and engineered biointerfaces with tailorable functionalities.

3:00pm **BI+AS-MoA3 Molecular-Level Surface Analysis Demonstrates the Impact of Detergent Selection on Decellularized Tissues**, ***Adam Taylor***, University of Washington, *L.J. White,* University of Nottingham, UK, *D.M. Faulk, L.T. Saldin,* University of Pittsburgh, *D.G. Castner,* University of Washington, *S.F. Badylak,* University of Pittsburgh, *B.D. Ratner*, University of Washington

Decellularized matrix scaffolds may be prepared through a range of techniques. Detergents are frequently used in decellularization protocols due to their ability to solubilize cell membranes and dissociate DNA from proteins. Whilst removal of cellular material is regularly assessed, the impact of detergent selection on extracellular matrix (ECM) structure and composition is less commonly investigated. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a powerful surface analysis technique to probe biological structures with high mass resolution and surface specificity, and has previously been used to distinguish decellularized ECM by anatomical location or culture conditions. The objective of this study was to utilize ToF-SIMS to investigate the influence of detergent selection upon a representative decellularized tissue, specifically the basement membrane complex (BMC) of porcine urinary bladder matrix (UBM) prepared by treatment with 1% SDS, 4% deoxycholate, 8 mM CHAPS or 3% Triton X-100 for 24 hours.

Principal components analysis (PCA) revealed spectral differences between treatment groups. High mass peaks associated with specific detergent fragments were observed on the scaffolds exposed to SDS and deoxycholate. Peaks indicative of phospholipid membranes were observed in all samples, but to a greater extent with scaffolds not exposed to detergent. We further probed these data sets to investigate how detergent selection impacts proteinaceous ECM components. Using a reduced peak list of known characteristic amino acid fragments, PCA distinguished native bladder tissue from decellularized UBM and highlighted spectral differences between UBM treated with ionic vs. charge-neutral detergents. Notably, the basement membrane surface of UBM prepared with ionic detergents SDS and deoxycholate yielded less intense characteristic peaks from hydrophobic amino acids than UBM treated with charge neutral detergents CHAPS and Triton X-100. Harsher detergents may denature protein structure and break protein-protein interactions through binding of their hydrophobic tail to hydrophobic amino acid residues. Such damage is hypothesized to cause sub-optimal in vitro and in vivo responses. We further examined cell-matrix interactions of human urothelial cells seeded on the BMC of UBM, investigating how detergent exposure affected cell proliferation and permeability of the cell monolayer. An understanding of the effects of detergent exposure on the structure, composition and surface molecular functionality of decellularized scaffolds will facilitate a rational strategy for successful recellularization and subsequent positive clinical outcomes.

3:20pm **BI+AS-MoA4 Liquid Repelling Surfaces Based on Candle Soot are Non-Fouling**, ***Lars Schmüser***, *M. Paven, N. Encinas,* Max Planck Institute for Polymer Research, Mainz, Germany, *D.J. Graham, D.G. Castner,* University of Washington, *D. Vollmer, H.J. Butt, T. Weidner*, Max Planck Institute for Polymer Research, Mainz, Germany

Super non-fouling surfaces resist protein adhesion and have a broad field of possible application like implant technology, drug delivery, blood compatible materials, biosensors and marine coatings. Non fouling properties can be fabricated by using liquid repelling surfaces, which minimize the contact area of water soluble particles with the non fouling surface. For a surface to be "amphiphobic" – to repel a range of liquids including oil and water – requires a micro to nanometer scale surface roughness in combination with a hydrophobic coating. Paven et al. (*1*) described the production of an amphiphobic surface with remarkably low production requirements. This surface is made of a glass slide, candle soot

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*** ASSD Student Award Finalist**

and 2 commercially available chemicals which are deposited via chemical vapor deposition. Soot deposition and chemical vapor deposition can be applied to a broad variety of substrate shapes, such as the inner wall of tubes. This makes the soot coating a promising tool for blood compatible material design for stents and tubing including applications such as dialysis. Here we present a protein adsorption study onto these amphiphobic surfaces made of candle soot. Since even nanograms per cm^2 levels of protein on biomaterial surfaces can cause detrimental effects for patients, we employed surface sensitive spectroscopic methods, X-ray photoelectron spectroscopy (XPS) and time of flight secondary ion mass spectrometry (ToF-SIMS) to quantify protein adsorption. We did not detect any adsorbed proteins within a detection limit of better than 1 ng/cm² of adsorbed proteins, which demonstrates the super non-fouling property of soot-coated surfaces. Interestingly, the naturally amphiphobic cuticle ("skin") of springtails – small ancient arthropods who live in soil – use an approach very similar to the artificial soot surfaces to achieve protein repellency: Nanometer roughness with hydrophobic coatings. We will discuss XPS, ToF-SIMS and fluorescence microscopy studies quantifying the amount of protein adsorbed onto these surfaces.

1. M. Paven *et al.*, Super liquid-repellent gas membranes for carbon dioxide capture and heart–lung machines. *Nat Commun*4, (2013).

3:40pm **BI+AS-MoA5 Time-of-Flight Secondary Ion Mass Spectrometry Investigations of the Pancreatic Islet Tumor Microenvironment**, ***Blake Bluestein***, Department of Bioengineering, University of Washington, *F.M. Morrish, D. Hockenbery,* Fred Hutchinson Cancer Research Center, *L.J. Gamble*, Department of Bioengineering, University of Washington

Imaging time-of-flight secondary ion mass spectrometry (ToF-SIMS) provides chemical information with subcellular spatial resolution. In this work, imaging ToF-SIMS is used to analyze tumor microenvironments from mouse model (Myc/p53-/-) biopsies with Myc-dependent inducible and regressible pancreatic β-cell neoplasia. The Myc oncogene is overexpressed in many human cancers and has major effects on cellular metabolism, including lipid metabolism. While imaging ToF-SIMS analysis of tumor tissue will provide a new perspective by visualizing tumor progression/regression, the system itself can also act as a model system for investigating stroma-tumor interactions in cancerous tissues.

Pancreatic tissues were harvested and frozen in optimal cutting temperature (OCT) at 6 days post Myc induction. 4 µm cryosections were serially cut, with one used for H&E staining, one for ToF-SIMS analysis, and another for immunohistochemistry. High mass and high spatial resolution data was acquired with the pulsed 25 keV Bi$_3^+$ ion beam rastered over a 1 mm x 1 mm area (1280 x 1280 pixels). ROIs of the tumor and stromal tissue were then investigated further with imaging principal components analysis (PCA) to identify peaks that correspond to species of interest. Regions identified by analysis and PCA were cross-referenced against immunohistochemical and H&E images to differentiate tumor areas from the surrounding tissue.

ToF-SIMS data suggests a preferential uptake of fatty acids 18:3 and 18:2 within the tumor. The 6 day Myc-induced islet tumor exhibits a signal of 14:0, possibly a product of de novo fatty acid synthesis within the tumor. The tumor also exhibits an increased localization of sphingomyelin fragments and vitamin E compared to the surrounding tissue. Interestingly, the data shows an absence of Mg$^+$ within the islet tumor and small, higher signal regions on the periphery of the tumor. These peripheral tumor regions also show an increased, localized signal of CN$^-$, CNO$^-$, C$_7$H$_{10}$O$^+$, and Fe$^+$, but further histologic correlations are needed to discern if these structures are inflammatory zones, mitochondrial dense regions, or related to vasculature. Once these localized areas have been defined, a comparison to the chemistry identified by ToF-SIMS may aid in interpreting the Myc oncogene and its effect on pancreatic β-cell neoplasia. PCA was applied to image data and revealed different chemistries within the tumor and surrounding tissue. PCA was also applied to selected tumor region images to spatially and chemically analyze within the tumor to compare chemistries between different tumor sizes, where tumor size is potentially indicative of different tumor stage development.

4:00pm **BI+AS-MoA6 Paper-based Device for Home Phenylalanine Monitoring from a Sample of Whole Blood**, *R. Robinson*, ***Elain Fu***, Oregon State University

Paper microfluidics is a rapidly growing subfield of microfluidics that makes use of paper-like porous materials to create devices for use in low-resource settings. Advantages of the use of porous materials include capillary flow, removing the need for equipment for pumping fluids, and lower material costs compared to traditional microfluidics-based devices composed of silicon or glass. In the current presentation, we describe the development of a paper-based device for home therapy monitoring. For persons with phenylketonuria (PKU), maintaining a restricted level of phenylalanine (Phe) in the body is a continuing challenge. Given the large inter-person variation in Phe metabolism, maintaining nutritional therapy can be a lengthy and difficult process that would be aided by the ability to perform real-time monitoring of Phe levels. Adherence to diet therapy is an even greater challenge for young children, adolescents, and women during pregnancy, and for these groups in particular, rapid feedback could be critical in tailoring a diet to be optimal for each individual. Current tests for Phe require a high-resource laboratory environment and are not suitable for the rapid detection of Phe levels and feedback to the patient that is needed for effective monitoring of PKU therapy. Our solution is a semi-quantitative, paper-based device that is rapid, easy to use, and low cost for patient home use. Device operation is based on simple user steps. The user applies whole blood (40 mL) to a plasma separation membrane, which filters out the cellular components of the blood and releases plasma to two downstream glass fiber pads. There, Phe in the sample and NAD+, catalyzed by the enzyme phenylalanine dehydrogenase, react to form Phe-pyruvate, NADH, and NH$_3$. At 6 min, the user folds the card closed and fluid is transferred to a final glass fiber detection pad, in which NADH, nitroblue tetrazolium, and methoxy phenazine methosulfate react to form NAD+ and a purple-colored product. The device is read at ~7.5 min. Visibly distinct signal intensities are generated from whole blood samples containing 0 (normal), 3.75 (slightly elevated), and >7.5 mg/dL (substantially elevated) spiked-in Phe. Thus, this test may allow users to distinguish between normal versus elevated levels of blood Phe on a rapid timescale that could inform their diet therapy. The assay exhibited reasonable reproducibility with coefficients of variation between 11 and 24%. A focus of the presentation will be on the controled patterning and drying of biochemical reagents in porous materials for later rehydration on the device, which is key to the robust operation of the device.

4:20pm **BI+AS-MoA7 Multivalent Probes for Tuneable 'Superselective' Targeting**, *G.V. Dubacheva,* CIC biomaGUNE, Spain, *T. Curk,* University of Cambridge, UK, *R. Auzély-Velty,* Cermav, Cnrs, France, *D. Frenkel,* University of Cambridge, UK, ***Ralf Richter***, CIC biomaGUNE & University Grenoble Alpes, Spain **INVITED**

A basic requirement in biomedical research is the ability to specifically target cells and tissues. Targeting typically relies on the specific binding of a 'ligand' on a tailor-made probe to a 'receptor' on the desired cell or tissue. Conventional probes efficiently distinguish a cell surface displaying the receptor from others that do not. They exhibit limited selectivity, however, when the surfaces to be distinguished display a given receptor at different densities.

Based on theoretical arguments, it has been proposed that multivalent probes that bind several receptors simultaneously can sharply discriminate between different receptor densities. Here, we present an experimental model system that demonstrates such 'superselective' targeting. To this end, recent achievements of synthetic chemistry and surface characterization were combined to create well-defined multivalent polymers and surfaces that interact with each other through highly specific host/guest interactions. With this model system, we show that superselective binding can be tuned through the design of the multivalent probe to target a desired density of binding sites. We develop an analytical model that provides simple yet quantitative predictions to tune the polymer's superselective binding properties by its molecular characteristics such as size, valency, and affinity.

This work opens up a route toward the rational design of multivalent probes with defined superselective targeting properties for practical applications in life sciences (analytics, diagnostics and therapy). It also provides mechanistic insight into the regulation of multivalent interactions in biology, notably the superselective targeting of the extracellular matrix polysaccharide hyaluronan to its main cell surface receptor CD44.

5:00pm **BI+AS-MoA9 Targeted Ultrathin Silica Nanoshells as HIFU Sensitizing Agents for *In Vivo* LnCAP Prostate Tumor Removal**, ***James Wang***, *A. Liberman, C. Barback, S. Blair, R. Mattrey, W. Trogler, A.C. Kummel*, UC San Diego

Diagnostic ultrasound (US) is a prevalent medical imaging modality due to its low-cost, high resolution, and therapeutic capability when coupled with high intensity focused ultrasound (HIFU) systems. 500 nm rigid silica ultrathin nanoshells were synthesized as a chemically stable US tumor marking contrast agent with continuous *in vivo* US imaging lifetime. Iron (III) was included into the silica shell network to promote biodegradability from serum transferrin proteins. It was shown previously that the removal of iron from the silica shell network via transferrin fragments the nanoshells for effective biodegradation. Folate was conjugated to the surface of the silica nanoshells via the 3-aminopropyltriethoxysilane (APTES) linker. Folate has been shown in the literature to bind to prostate specific membrane antigen (PSMA) with a high binding affinity due to folate hydrolase activity. Conjugating the silica nanoshell surface with folate targets the ultrathin silica nanoshells towards the LnCAP tumor where PSMA is significantly up-regulated. The surface modified ultrathin silica nanoshells were filled with liquid perfluorocarbon (PFC) which underwent acoustic droplet vaporization (ADV) during US insonation. The phase transition of PFC from liquid to vapor generated a large amount of PFC microbubbles that created contrast during US imaging. *In vitro* experiments with US have demonstrated that the ultrathin silica nanoshells can be imaged for at least 3 hours under color Doppler imaging, exhibiting a continuous US imaging lifetime. *In vivo* experiments have shown that folate conjugated silica nanoshells were able to accumulate and persist within the tumor region for up to 12 days post-injection, observable with US imaging. Surface conjugation with polyethylene glycol (PEG) increased the ultrasound signal at the tumor by increasing the particles accumulating at the tumor site. When exposed to high intensity focused ultrasound (HIFU), the particles were able to enhance the HIFU power and liquefy tumor tissue. With particles present, the HIFU duty cycle can be lowered to 2 %, minimizing tissue thermal deposition. By synthesizing ultrathin silica nanoshells with a folate-conjugated surface, it is has been demonstrated that folate-conjugated ultrathin rigid silica nanoshells can accumulate in the LnCAP tumor persistently for 12 days. PEGylation of the particles further increase the particle accumulation concentration in the tumor, acting as a HIFU sensitizing agent for ultrasound histotripsy. Through intelligent surface modification, liquid PFC filled silica particles can act as a multi-functional theranostic agent for ultrasound diagnosis.

5:20pm **BI+AS-MoA10 Transparent Field Effect Sensor with Nanostructured Amorphous In-Ga-Zn-O Wires***, **Xiaosong Du**, Y. Li, J. Motley, G. Herman*, Oregon State University

Amorphous In-Ga-Zn-O (a-IGZO) materials have a wide range of applications in high performance electronic devices, from the active material in thin film transistors for flat-panel displays and as the transducer for field effect sensors. A key benefit of a-IGZO over amorphous silicon is that it enables low processing temperatures, while retaining relatively large electron mobilities, low operating voltages, and very low off currents. In this study, we have fabricated a-IGZO films with well-defined nanostructures using colloidal lithography. These nanostructured a-IGZO films were then patterned into wires using electrohydrodynamic printing of an etch resist followed by wet chemical etching. We have characterized these nanostructured a-IGZO wires using field effect test structures to evaluate their electronic properties. To improve selectivity and stability of the nanostructured a-IGZO wires for sensing applications we have functionalized the back-channel surface with molecular receptors, where glucose oxidase was successfully attached as a sensing enzyme. Depletion/accumulation of carriers in the a-IGZO back-channel was observed upon reaction of the glucose oxidase with the analyte, which leads to significant changes in the sensors electronic signals. Continuous monitoring of glucose concentration can be achieved by measuring a direct change in channel conductance, turn on voltage shift, and/or electrical hysteresis. The results obtained for nanostructured a-IGZO wires will be compared to blanket a-IGZO films, where we have found that the nanostructured a-IGZO wires provide a significant enhancement in sensitivity to subtle changes in glucose concentrations in physiological buffers. These results provide insight into a route to develop low-cost transparent biochemical sensors based on the emerging a-IGZO technology.

Electronic Materials and Processing
Room: 211A - Session EM+AS+SS-MoA

MIM Diodes, Functional Oxides, and TFTs
Moderator: Pat Brady, RedWave Energy, Inc., John Conley, Oregon State University

2:20pm **EM+AS+SS-MoA1 Engineered Tunnel-Barrier Terahertz Rectifiers for Optical Nantennas***, **Ivona Mitrovic**, N. Sedghi, A.D. Weerakkody, J.F. Ralph, S. Hall, J.S. Wrench, P.R. Chalker,* University of Liverpool, UK, *Z. Luo, S. Beeby*, University of Southampton, UK

Thin film metal-insulator-metal rectifying devices using double, triple or quadruple insulator layers are currently the focus of attention for the development of next-generation optical nantennas for infrared energy harvesting. The interest is driven by their distinctive attributes, such as nanoscale footprint, room temperature operation, zero bias voltage requirement, and ease of integration with Complementary Metal Oxide Semiconductor technology. Highly asymmetric and nonlinear current-voltage (IV) behaviour at low applied voltages is critical for this application. In this paper, we present comprehensive experimental and theoretical work on tunnel-barrier rectifiers comprising double (Ta_2O_5/Al_2O_3 and Nb_2O_5/Al_2O_3) and triple ($Ta_2O_5/Nb_2O_5/Al_2O_3$) insulator configurations engineered to enhance low voltage nonlinearity. There are two mechanisms that allow metal-insulator-insulator-metal (MIIM) rectifiers to have a high nonlinearity while keeping the resistance low: (i) resonant tunnelling, and (ii) step tunnelling. This paper focuses on the former approach. A modified multi-layer Tsu-Esaki method has been used for IV calculations from the transmission coefficient by the transmission matrix method. The theoretical work indicates that the onset of resonant tunneling in MIIM and MIIIM rectifiers can be adjusted to be close to zero volts by appropriate choice of work function difference of the metal contacts, the thickness of insulator layers, and the depth of the quantum well. The double and triple insulator rectifiers were fabricated using atomic layer deposition (ALD) and rf magnetron sputtering, while different metal contacts including Al, Ta, W, Nb, Cr and Ag were defined by photolithography or shadow mask and deposited by e-beam and thermal evaporation. The thickness, band gap, surface roughness, band offsets and work functions have been extracted from variable angle spectroscopic ellipsometry, atomic force microscopy, x-ray and inverse photoelectron spectroscopy on fabricated devices to ascertain the quality of the interfaces and to measure barriers. The key rectifier properties, asymmetry, nonlinearity and responsivity have been assessed from current voltage measurements performed in the range 293-370 K. A superior low voltage asymmetry (18 at 0.35 V) and responsivity (9 A/W at 0.2 V) has been observed for fabricated bilayer Ta_2O_5/Al_2O_3 and Nb_2O_5/Al_2O_3 MIIM devices respectively, in advance of state-of-the-art experimental values. The results demonstrate ALD and rf sputtered tunnel-barrier rectifiers which enhance low voltage nonlinearity and have the potential to be employed in optical nantennas for infrared energy harvesting.

2:40pm **EM+AS+SS-MoA2 MIM Diodes for RF Energy Harvesting***, A.A. Khan, A. Syed, F. Ghaffar, **Atif Shamim***, King Abdullah University of Science and Technology

Metal Insulator Metal (MIM) diodes that work on fast mechanism of tunneling have been used in a number of very high frequency applications such as (Infra Red) IR detectors and optical Rectennas for energy harvesting. Their ability to operate under zero bias condition as well as the possibility of realizing them through additive techniques makes them attractive for (Radio Frequency) RF applications. However, two major issues namely, high surface roughness at the metal-insulator junction which effects the reliability of the diode, and very high resistance (typically in Mega Ohms) which complicates its matching with RF antenna have prevented its wide spread use in RF rectennas.

In this work, various metal deposition methods such as sputtering and electron beam evaporation are compared in pursuit of achieving low surface roughness. Amorphous metal alloy has also been investigated in terms of its low surface roughness. Zinc oxide has been studied for its suitability as a thin dielectric layer for MIM diodes. Finally, comprehensive RF characterization of MIM diodes has been performed in two ways: 1) by standard S-parameter methods, and 2) by investigating their rectification ability under zero bias operation.

It is concluded from the Atomic Force Microscopy (AFM) imaging that surface roughness as low as sub 1 nm can be achieved reliably from crystalline metals such as copper and platinum. This value is comparable to surface roughness achieved from amorphous alloys, which are non-crystalline structures and have orders of magnitude lower conductivities. Relatively lower resistances of the order of 1 Kilo Ohm with a sensitivity of 1.5 V^{-1} have been obtained through DC testing of devices with MIM diode structure of platinum/zinc oxide/ titanium. Finally, RF characterization reveals that input impedances in the range of 300 Ω to 25 Ω can be achieved in the low GHz frequencies (from 0.5-10 GHz). From the rectification measurements at zero bias, a DC voltage of 4.7 mV has been obtained from an incoming RF signal of 0.4 W at 2.45 GHz, which indicates the suitability of these diodes for RF rectenna devices without providing any bias. These preliminary results indicate that with further optimization, MIM diodes are attractive candidates for RF energy harvesting applications.

3:00pm **EM+AS+SS-MoA3 Diode Structure Based on Carbon Materials for Ultra high Frequency Driving***, **JaeEun Jang***, Daegu Gyeongbuk Institute of Science and Technology (DGIST), Republic of Korea

If the antenna can be designed to absorb wavelengths in the range of a few hundred THz with multi-antenna array design, it results in high conversion efficiency due to power production from various light sources between ultraviolet (UV) and infrared (IR) radiation that is often thought of as heat and exists beyond the visible range for humans. One of the problems in this idea, however, is the nature of visible or IR light to oscillate at ultra-high frequencies. Therefore, a rectifier working at such an ultra-high frequency should be developed with a highly efficient coupling between antenna and light. Because Schottky diode is limited to frequencies less than ~ THz level, nanometer size MIM diode structure has been suggested as alternative design. Two different metals have used normally to make an asymmetric characteristic of current-voltage. However the work function difference between the metals cannot produce a high asymmetry, which causes a poor rectifier performance, even though the structure can be driven in THz range. To solve this issue, we used a structural asymmetric MIM design. The planar asymmetric design using various metals or grapheme showed better asymmetric I-V characteristics than that of simple MIM structure. In addition, for the vertical aligned design, single multi-wall carbon nanotube was formed as one electrode to get high tunneling current caused by the structural effect of sharp tip. The structural asymmetry can make a different field density states to the metals, which induces a high rectify characteristics. The contrast ratio between the forward and the reverse bias is $\sim 10^4$ level. The estimated cut-off frequency is about 4.74THz. The electrical characteristics are stable up to 423K.

3:20pm **EM+AS+SS-MoA4 Optical Rectenna Arrays using Vertically Aligned Carbon Nanotubes**, ***Baratunde Cola***, Georgia Institute of Technology

The response of a multiwall carbon nanotube to visible light has been reported to be consistent with conventional radio antenna theory. Researchers have proposed that this result might be exploited to realize an optical rectification device – that is, a device that converts free-propagating electromagnetic waves at optical frequencies to localized d.c. electricity. However, an experimental demonstration of this concept requires that the multiwall carbon nanotube antenna be coupled to a diode that operates on the order of 1 petahertz (switching speed on the order of a femtosecond). Ultralow capacitance, on the order of a few attofarads, could allow a diode to operate at these frequencies; and the development of metal-insulator-metal tunnel junctions with nanoscale dimensions has emerged as a potential path to diodes with ultralow capacitance, but these structures remain extremely difficult to fabricate and couple to a nanoscale antenna reliably. Here we demonstrate optical rectification by engineering metal-insulator-metal tunnel diodes at the tips of multiwall carbon nanotubes, which act as the antenna and metallic electron emitter in the diode. This performance is achieved using diode areas based on the diameter of a single carbon nanotube (about 10 nanometers), geometric field enhancement at the carbon nanotube tips, and a low work function semi-transparent top metal contact. Using vertically-aligned arrays of the diodes, we measure d.c. open-circuit voltage and short-circuit current at visible and infrared electromagnetic frequencies that is due to a rectification process, and quantify minor contributions from thermal effects. Our devices show evidence of photon-assisted tunneling, and exhibit zero-bias diode responsivity on the order of 0.1 amps per Watt and zero-bias differential resistance as low as 100 ohms-centimeter squared under illumination. Additionally, power rectification is observed under simulated solar illumination. Numerous current-voltage scans on different devices, and between 5-77 degrees Celsius, show no detectable change in diode performance, indicating a potential for robust operation.

3:40pm **EM+AS+SS-MoA5 World Record Tunable Microwave Dielectrics**, *C.H. Lee,* Cornell University, *N.D. Orloff,* National Institute of Standards and Technology (NIST), *T. Birol, Y. Zhu, Y. Nie,* Cornell University, *V. Goian,* Institute of Physics ASCR, *R. Haislmaier,* Pennsylvania State University, *J.A. Mundy,* Cornell University, *J. Junquera,* Universidad de Cantabria, *P. Ghosez,* Université de Liège, *R. Uecker,* Leibniz Institute for Crystal Growth, *V. Gopalan,* Pennsylvania State University, *S. Kamba,* Institute of Physics ASCR, *L.F. Kourkoutis, K.M. Shen, D.A. Muller,* Cornell University, *I. Takeuchi,* University of Maryland, College Park, *J.C. Booth,* National Institute of Standards and Technology (NIST), *C.J. Fennie,* ***Darrell Schlom***, Cornell University **INVITED**

The miniaturization and integration of frequency-agile microwave circuits—relevant to electronically tunable filters, antennas, resonators, phase shifters and more—with microelectronics offers tantalizing device possibilities, yet requires thin films whose dielectric constant at GHz frequencies can be tuned by applying a quasi-static electric field. Appropriate systems, e.g., $Ba_xSr_{1-x}TiO_3$, have a paraelectric-to-ferroelectric transition just below ambient temperature, providing high tunability. Unfortunately such films suffer significant losses arising from defects. Recognizing that progress is stymied by dielectric loss, we start with a system with exceptionally low loss—$Sr_{n+1}Ti_nO_{3n+1}$ phases—where $(SrO)_2$ crystallographic shear planes provide an alternative to point defect formation for accommodating non-stoichiometry. Guided by theoretical predictions, we biaxially strain a $Sr_{n+1}Ti_nO_{3n+1}$ phase with $n = 6$ to introduce a ferroelectric instability and create a new type of tunable microwave dielectric. This tunable dielectric exhibits a world record figure of merit at room temperature and frequencies up to 125 GHz. Our studies also reveal details about the microscopic growth mechanism of these phases, which are relevant to preparing atomically precise oxide interfaces to these and other Ruddlesden-Popper phases.

4:20pm **EM+AS+SS-MoA7 Bandgap Engineering and Application of SiZnSnO Amorphous Oxide Semiconductor**, ***Sang-Yeol Lee***, Cheongju University, Republic of Korea **INVITED**

The band gap of the amorphous SiZnSnO (SZTO) semiconductor has been controlled by bandgap engineering using Si ratio. The addition of small amount of Si in SZTO channel layer can change the position of Fermi level in band gap. By investigating the ultraviolet photoelectron spectroscopy (UPS) characteristics, it is verified that Si atoms can modify the Fermi energy level of SZTO thin films. Carrier generation originated from the oxygen vacancy could modify the Fermi level in the band gap of oxide thin films since Si could be an oxygen vacancy suppressor. This is also related with the origin of defect state which was observed to be involved with the creation of oxygen vacancies. Since it is not so easy to derive directly the change of the Fermi energy level in the energy band gap of amorphous oxide semiconductor, no report of the relation between the Fermi energy level in the energy band gap of oxide semiconductor and the device stability of oxide thin film transistors has been reported. We derive directly band gap and Fermi energy level by using the ultraviolet photoelectron spectroscopy (UPS) characteristics, Kelvin probe (KP) and electron energy loss spectroscopy (EELS). The instability mechanism of amorphous oxide thin film transistors based on the band parameter of oxide semiconductor will be discussed and applied to display applications.

5:00pm **EM+AS+SS-MoA9 Self-aligned Vertical ZnO-based Circuits by Spatial ALD**, ***Shelby Nelson***, *C.R. Ellinger, L.W. Tutt,* Eastman Kodak Company

Metal oxide thin-film transistors (TFTs) are becoming the mainstream for display backplanes. These TFTs are fabricated with traditional photolithographic techniques, typically on rigid substrates. In our lab, we explore approaches that are more "print-compatible", with broad alignment tolerance and no small-gap mask features. We deposit zinc oxide (ZnO) semiconductors, aluminum oxide (Al_2O_3) dielectrics, and aluminum-doped zinc oxide conductors by the fast, atmospheric pressure, large-area-compatible, spatial atomic layer deposition (SALD) process. In addition to depositing good-quality thin-film transistor layers at temperatures at and below 200 °C, this process can work with a wide variety of rough and deformable substrates.

Here we describe vertical TFT and circuit architectures that unite process simplicity with high performance. The liberal design rules result from vertical transistors with self-aligned source and drain contacts that define the sub-micron channel length. Using 10-micron design rules for both the minimum line/space dimensions and for alignment tolerances, we have fabricated 9-stage ring oscillators with greater than 1 MHz oscillation frequency, at supply voltage below 6 V. Starting with a gate layer with a re-entrant profile on the edge, these devices use spatial ALD to conformally coat the Al_2O_3 gate dielectric and ZnO semiconductor, and a line-of-sight deposition process such as evaporation for the aluminum electrodes. Individual device characteristics as well as circuit performance will be discussed.

5:20pm **EM+AS+SS-MoA10 Geometrically Asymmetric Tunneling Nanostructures by Atomic Layer Deposition**, ***Jie Qi***, *X. Jiang, B.G. Willis*, University of Connecticut

Geometrically asymmetric tunneling nanostructures are of interest to make ultra-high frequency diodes for applications in detection and solar energy harvesting. Atomic layer deposition (ALD) is one of the most promising techniques for fabrication of tunneling nanostructures. In previous work, it has been demonstrated that individual metal-vacuum-metal (MVM) tunnel junctions with a gap distance of 1-2 nm can be fabricated by selective-area ALD of Cu onto Pd templates. However, optimizing nonlinearity and scaling up to large arrays of tunneling devices both introduce new challenges that include achieving precise control of nucleation and good quality conformal growth on sharply defined asymmetric nanostructures.

In this study, the fabrication of large arrays of MVM tunnel junctions is investigated using selective-area ALD. Nano-patterned Pd nanostructures with sharp asymmetric features are prepared as seed layers for planar, geometrically-asymmetric junctions on SiO_2 / silicon substrates by high-resolution electron beam lithography. Selective-area ALD applied to patterned Pd nanostructures allows tuning the size of junctions to nanometer dimensions. Microscopy and chemical analysis are used to evaluate nanostructure morphology, tunnel junction uniformity, and selective area growth characteristics. In-situ electrical measurements are used to measure DC current-voltage curves and nonlinearity. It was found that film nucleation and growth selectivity can be greatly affected by different pre-deposition sample treatments. UV/Ozone (UVO) cleaning and hydrogen annealing before ALD both enhance the nucleation of Cu thin films on Pd seed layers. In addition, UVO treatment promotes selective growth on Pd vs. SiO_2 areas while boiling samples in water to hydroxylate SiO_2 surface area contributes to a loss of selectivity. In-situ measured electrical data during ALD growth demonstrate a gradual convergence to tunneling with sub-nm control provided by the ALD method. However, control of tunneling non-linearity and geometric asymmetry is complicated by an incomplete understanding of the growth mechanism and the morphology evolution of nanostructures. There is a compromise between conditions that promote good ALD growth and those that maintain geometric asymmetry. We conclude with suggestions to promote growth, maintain sharp asymmetric features, and achieve non-linear tunneling characteristics.

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, SiGeOx, 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 identity 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 ~ $3x10^{11}$ ($eV^{-1}cm^{-2}$).

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_3N_4 growth on Si(100) by hydrazine and Si_2Cl_6 at temperatures in excess of 350°C with solid ammonium chloride by-product formation[1]. The first half reaction of N_2H_4 leaves N-H_x surface termination, and the second reaction with Si_2Cl_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_2Cl_6 dose followed by 17 cycles of 3 MegaLangmuir hydrazine and 3 MegaLangmuir Si_2Cl_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_2O_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_2O_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_2O_2 and 32373ppm for water, where the H_2O/H_2O_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_2NNH_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_2O_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 $E_1+\Delta_1$ 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 $E_1+\Delta_1$ 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 $E_1+\Delta_1$ 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 ($4x10^{-3}$-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 ($<4x10^{-3}$ $cm^2V^{-1}s^{-1}$) 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.

Work supported by the NSF under DMR-1309642, in addition to the University of Minnesota NSF MRSEC under DMR-1420013.

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.

IPF on Mesoscale Science and Technology of Materials and Metamaterials
Room: 210F - Session IPF+MS-MoA

Mesoscale Phenomena in the Biosciences II (2:20-3:40) & Metamaterials (3:40-5:40)
Moderator: Carolyn Larabell, University of California, San Francisco, Mark Brongersma, Stanford University

2:20pm **IPF+MS-MoA1 Mesoscale Imaging in Cell Biology**, ***Gerry McDermott***, *M. Do, J.-H. Chen, A. Walter, M.A. Le Gros, C.A. Larabell*, University of California, San Francisco **INVITED**

Soft X-ray tomography (SXT) is ideally suited to imaging the sub-cellular architecture of biological cells. In SXT, specimens are illuminated with 'water window' photons. X-rays within this energy range (284 – 543eV) are absorbed an order of magnitude more strongly by carbon- and nitrogen-containing organic materials than by water. Consequently, the variation in biomolecule composition and concentration within the specimen gives rise to quantitative, high-contrast images of intact, fully hydrated cells, without the need to use contrast-enhancing agents. The utility of SXT has recently been enhanced by the development of high numerical aperture cryogenic fluorescence tomography (CFT) for correlated imaging studies. This multi-modal approach allows labelled molecules to be localized in the context of a high-resolution 3-D tomographic reconstruction of the cell. This talk will describe correlated CFT-SXT and the application of this technique to long-standing questions in cell biology.

3:00pm **IPF+MS-MoA3 Biomimetic Material Approaches to Tissue Engineering, Regenerative Medicine, and Wound Healing**, ***Elizabeth Loboa***, UNC-Chapel Hill & NC State University **INVITED**

There is growing clinical need in wound healing, tissue engineering, and regenerative medicine for controlled release systems that encapsulate therapeutic compounds and provide sustained release in a site-specific manner. Biocompatible, biodegradable nanofibrous scaffolds with their morphological similarities to the natural extracellular matrix (ECM) in vivo, high surface area to volume ratio, and small interfibrous pore sizes hold great potential for this application. Loading dopants within an electrospun polymeric matrix allows for consistent entrapment throughout the nanofibers. Further, the high surface area to volume ratio of these matrices maximizes the interaction of the carrier with a surrounding medium. A critical parameter for achieving success in controlled release is controlled diffusion of molecules out of the electrospun scaffolds. The drug release characteristics of nanofibrous scaffolds rely on how well the drug is encapsulated inside the nanofibers. These characteristics are critically affected by fiber morphology.

In this presentation, Dr. Loboa will discuss approaches in her lab to elucidate and optimize biomimetic fibrous systems for wound healing, tissue engineering, and regenerative medicine applications. Focus will be placed on regeneration of skin and musculoskeletal tissues and approaches to wound care and tissue regeneration while combating multi-drug resistant bacteria.

3:40pm **IPF+MS-MoA5 Structured Light and Structured Surface Waves from Metasurfaces**, ***Federico Capasso***, Harvard University **INVITED**

Patterning surfaces with subwavelength spaced metallo-dielectric features (metasurfaces) allows one to locally control the amplitude, phase and polarization of the scattered light, allowing one to generate complex wavefronts such as optical vortices of different topological charge and dislocated wavefronts. 1,2 Recent results on achromatic metasurfaces will be presented including lenses and collimators. Metasurfaces have also become a powerful tool to shape surface plasmon polaritons (SPPs) and more generally surface waves. I will present new experiments on imaging SPP that have revealed the formation of Cherenkov SPP wakes and demonstrated polarization sensitive light couplers that control the directionality of SPP and lenses which demultiplex focused SPP beams depending on their wavelength and polarization.

1. N. Yu and F. Capasso Nature Materials 13, 139 (2014)

2. P. Genevet and F. Capasso Reports on Progress in Physics 78, 24401 (2015)

4:20pm **IPF+MS-MoA7 Quest for Extreme Photonics**, ***Nader Engheta***, University of Pennsylvania **INVITED**

Waves can be tailored, manipulated and sculpted by materials. Recent development in condensed matter physics, nanoscience, and materials science and technology has made it possible to construct materials and structures with unusual "extreme" characteristics. These "extreme" scenarios in light-matter interaction may come in several forms: It may be due to extreme in dimensionality such as metasurfaces and one-atom-thick materials, extreme near field such as subwavelength nonreciprocal vortexes in near zones of plasmonic structures, extreme anisotropy in design of superlattices with anisotropic effective mass of charged carriers, giant nonlinearity in phase-change dynamics, extreme information processing as in optical metatronics and "informatic" metastructures, and extreme material parameters such as epsilon- and/or mu-near-zero (ENZ, MNZ, and EMNZ) features leading to phenomena of "static optics". Such "extreme photonics" may provide us with exciting functionalities in both wave physics and quantum optics and engineering. In this talk, some of our ongoing work in these areas will be discussed along with some of the opportunities and challenges in this area.

5:00pm **IPF+MS-MoA9 2D Materials: Graphene and Beyond**, ***Tony Heinz***, Stanford University **INVITED**

The past few years have witnessed a surge of activity in the study of graphene and, more recently, in other atomically thin two-dimensional materials. We will describe some the reasons for the intense interest in these new material systems, highlighting their unusual electronic properties. We will show how we can use light to probe the distinctive properties electrons in model 2-D materials such as graphene and transition metal dichalcogenides. We will discuss the basics of light-matter interactions in these 2-D materials, as well as signatures of electron-electron and electron-phonon interactions, describing both the fascinating physics of these material systems and emerging applications in photonics.

In-Situ Spectroscopy and Microscopy Focus Topic
Room: 211C - Session IS+AS+SA+SS-MoA

Ambient Pressure X-ray Photoelectron Spectroscopy Studies for Catalytic and Energy Materials in Gas Phase

Moderator: Peter Crozier, Arizona State University, Franklin (Feng) Tao, University of Kansas

2:20pm **IS+AS+SA+SS-MoA1 In situ Electron Spectroscopy for Energy Science**, ***Robert Schlögl***, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany **INVITED**

The use of volatile renewable electricity in lager amounts in our energy systems requires grid-scale technologies for integration electricity in material energy carrier streams. Several systemic options always suffer from our conceptual weakness to convert free electrons in chemical bonds. This can be achieved with accumulators for limited applications and should be done through water splitting and synthesis of solar fuels in almost unlimited applications. Complex interfacial chemistry is the underlying scientific challenge. To tackle this old challenge with new concepts it is essential to improve our ability to study chemical, electronic and geometric structures of nanoscopic objects in-situ meaning under operation conditions. A whole train of dedicated instrumentation from specimen formation, data acquisition and auxiliary analyses plus sample manipulation is necessary for this task. The presentation gives some aspects of priority challenges and uses examples of operation studies of water splitting catalysts and of CO2 reduction systems to illustrate the present status of insight. In the outlook the possibilities of the novel experiment EMIL at BESSY will be discussed.

3:00pm **IS+AS+SA+SS-MoA3 Catalysis on Singly Dispersed Bimetallic Sites on Oxide Support**, ***Luan Nguyen***, University of Kansas, *A. Frenkel*, Yeshiva University, *J. Li*, Tsinghua University, China, *F. Tao*, University of Kansas

Reaction events of heterogeneous catalysis occur on specific catalytic sites. Atoms of a catalytic site arrange in a specific geometric/electronic configuration for adsorbing/dissociating reactant molecules and subsequent coupling to form product molecules. Bimetallic catalysts play significant roles in chemical and energy transformations due to their tunable catalytic properties through ligand, geometric, bi-functional, or lattice strain effect.

When a bimetallic site (M_1A_n, M and A: metal elements, $n \geq 1$) is one of the continuous sites on the surface of a bimetallic NP, this site is in a metallic state. However, when M_1A_n sites are *separately* anchored on a surface of a transition metal oxide support, these isolated bimetallic sites are in cationic state. Such change in electronic structure could cause these bimetallic sites to have stronger chemisorption to reactant or/and intermediate molecules, thus facilitating its dissociation and subsequent coupling. In addition, singly dispersion of metal M in M_1A_n minimizes the potential binding configurations of reactant molecules hence may enhance catalytic selectivity toward a specific reaction pathway. Here we present singly dispersed bimetallic catalyst Rh_1Co_3 prepared on Co oxide support, which exhibits 100% selectivity for the production of N_2 in NO reduction with CO.

Preparation of isolated bimetallic sites Rh_1Co_3 on Co_3O_4 nanorods begins with the formation of hydroxide species $Rh(OH)_n$ on the surface of Co_3O_4, followed by calcination at 150ºC in O_2 to form Rh-O-Co bonds between singly dispersed $Rh(OH)_n$ species and the surface of Co_3O_4, and concluded with a carefully controlled reduction to remove oxygen atoms between Rh and Co and thus a simultaneous formation of Rh-Co bonds. In-situ ambient pressure X-ray photoelectron spectroscopy (AP-XPS) was used to monitor the oxidation and reduction steps and to avoid over or under-reduction.

Formation of singly dispersed Rh atoms was visualized using HAADF-STEM. The bonding environment of Rh to three Co atoms was confirmed using in-situ EXAFS. For reduction of NO with CO, Rh_1Co_3/CoO exhibits high activity at 110 ºC with 100% selectivity toward N_2 production. In contrast, Rh-Co alloy NP/CoO has much lower activity and selectivity (10%) under the same condition. In-situ AP-XPS investigation shows that Rh atoms are at cationic state instead of metallic state. Along with this, DFT calculations suggest that a strong adsorption of intermediate N_2O molecules on Rh_1Co_3 site prevents its desorption as a byproduct and provides a dissociation pathway of N_2O to N_2 with a low activation barrier (~0.21 eV), thus leading to a 100% selectivity to N_2 production.

3:20pm **IS+AS+SA+SS-MoA4 Oxidation and Recovery of WC Thin Film Surfaces**, *E. Monazami,* University of Virginia*, J.B. McClimon,* University of Pennsylvania*, N. Johansson, P. Shayesteh, S. Urpelainen, J. Schnadt,* Lund University, Sweden*, **Petra Reinke***, University of Virginia

Transition metal carbide (TMC) surfaces are coveted as catalytic materials, electrodes and hard protective coatings. A bottleneck in their use is surface oxidation, which leads to a decay in performance. Our work establishes the feasibility of surface recovery by using a carbon-rich WC layer where recarburization of the surface is initiated by an annealing step. Thin carbon-rich tungsten carbide layers are grown by co-deposition of W and C_{60} on a MgO(001) surface at 1100 K. The MgO substrate serves as a diffusion barrier for carbon, and the films have a well-defined carbon inventory controlled by the deposition rates of the reactants. The film surfaces were studied by in-situ Scanning Tunneling Microscopy and Spectroscopy. Raman spectroscopy confirmed the presence of highly defective graphitic carbon. The oxidation-recarburization (O-R) cycles were studied in the ambient pressure endstation SPECIES at MAX-Lab (J. Synchr. Rad. 701, 19 (2012)) in a pressure of 0.3 mbar of O_2. Oxidation with $p(O_2)$ of 10^{-5} mbar were performed at SPECIES for direct comparison to low $p(O_2)$ STM experiments.

The carbon-rich WC films exhibit a relatively rough surface, which allows only in a few instances true atomic resolution, but graphite as well as graphene layers can be identified. Oxidation at T>550 K leads to etching of surface carbon and the growth of a W-oxide layer and STS maps show the oxide evolution. The oxidation in the low $p(O_2)$ pressure regime progresses slowly and the surface carbide is recovered by annealing.

The use of the SPECIES endstation enabled a quantiative study of the O-R cycles including a detailed analysis of the respective bonding environments which are modified at different times in the O-R cycle. The oxidation in the ambient pressure environment was monitored using the ratio of W-carbide to W-oxide in the W4f core level during the reaction. The steady state thickness of oxide is a function of sample temperature and order of annealing cycles. The surface carbide concentration can be fully recovered in a subsequent annealing step, and repeated O-R cycles were performed. The O-R process is controlled by the interplay between surface oxidation, oxygen and carbon diffusion and our results will be modeled with a simple set of transport equations. We will discuss the role of different bonding environments as we move through the O-R cycle and compare UHV and ambient pressure results up to 800 K. These results clearly illustrate that carbon-rich tungsten carbide materials can be used to achieve a long term use of carbide surfaces in catalysis and fuel cell applications.

supported by NSF-Division of Materials Research (Ceramics) DMR-100580, STINT award.

3:40pm **IS+AS+SA+SS-MoA5 Microscopy, Spectroscopy, and Reactivity of Surfaces in Vacuum and under Ambient Reaction Pressures**, ***Miquel Salmeron****, B. Eren*, Lawrence Berkeley National Laboratory **INVITED**

The goal of surface science research is to provide atomic level understanding of the structural and dynamic properties of surfaces, a goal particularly relevant for chemical applications, including catalysis, photochemistry, batteries and fuel cells. With X-ray Photoemision Spectroscopy (XPS) and X-ray absorption Spectroscopy (XAS) we determine composition and electronic structure. With Scanning Tunneling Microscopy (STM) we image atoms and molecules as they adsorb, diffuse and react on single crystal surfaces. To study surfaces in the presence of gases, in the Torr to Atmospheres range, which is relevant to practical catalysis, new instrumentation is needed. Over the last years we developed high pressure STM, XPS and XAS, to study surfaces under high coverage of adsorbates in equilibrium with gases near ambient pressures and temperature. Using a combination of these techniques I will show how under these conditions the structure of surfaces and the adsorbed layers can be very different from that at low coverage, or even at high coverage but at low temperature. Adsorbates can induce dramatic restructuring of the surface, as I will show in the case of CO induced restructuring of Cu surfaces and the reactions with Oxygen.

4:20pm **IS+AS+SA+SS-MoA7 Novel Solutions for Ambient Pressure and *In Situ* Photoelectron Spectro-Microscopy**, ***Hikmet Sezen****, M. Amati, L. Gregoratti*, Elettra-Sincrotrone Trieste, Italy

A technique based on photoelectron spectroscopy (PES) providing simultaneously spectroscopy and microscopy capabilities and being compatible with ambient pressure conditions is still missing. Ambient pressure PES (APPES), based on differential pumping of the electron energy analyzer, offers an optimal spectroscopic solution to overcome pressure barrier for surface related studies[1]. Unfortunately, APPES has very limited spatial resolution. On the other hand, a better than 100 nm spatial resolution scanning photoelectron microscope (SPEM), where the X-ray beam is demagnified down to a 130 nm spot by Zone Plate Fresnel optics and the sample scanned under the focused beam, is accessible from a few synchrotrons. A direct adaptation of the APPES approach to SPEM technique is not possible because of geometric constrains, stabilities and sustainability of the x-ray optics under near ambient pressures, and mechanical stability of the photoelectron detection system under such severe pumping conditions. In this presentation we will introduce two novel solutions for near-ambient pressure SPEM with ~100 nm spatial resolution and compatible with in-situ/operando conditions operated at ESCAmicroscopy beamline at Elettra synchrotron facility.

Dynamic high pressure (DHP) is the one of our near-ambient pressure SPEM solution. The technique is based on generating high pressure pulsed gas packets directed to the sample. Under influence of gas pulses the sample fells a few mbar pressure in a burst instant, then gas packets dilute into the SPEM chamber to yield a $1x10^{-5}$ mbar background pressure. From the test results a 10^{-3}-10^{-2} mbar equivalent static pressure was felt by Si and Rh samples during in-situ oxidation reaction.[2] It is available for users.

Effusive cell is another solution for near-ambient pressure SPEM. The sample is encapsulated with a vacuum sealed cell and located just 30-50 µm behind of a 200 µm diameter size pinhole. The focused x-ray beam are scanning the sample trough the pinhole. The generated photoelectrons come out from the same pinhole and are able to reach the electron energy analyzer. Due to the geometric orientation of energy analyzer and the pinhole we can achieve ca. a 200x100 μm^2 aerial point of view on the sample. The pressure inside the cell can be raised up to mbar range while the pressure in the main chamber kept around $1x10^{-5}$ mbar which is the safety limit for SPEM system. An encapsulated filament is behind the sample for heating, and other electrical connections are ready for biasing of sample, and thermocouple connections.

[1] D. F. Ogletree, et al. Rev. Sci. Instrum. 73, 3872 (2002)

[2] M. Amati, et al. J. Instrum. 8, 05001 (2013)

4:40pm **IS+AS+SA+SS-MoA8 *In Situ* Studies of Partial Oxidation of Methanol to Hydrogen on Isolated Bimetallic Site Pt_1Zn_n**, ***Shiran Zhang****, L. Nguyen,* University of Kansas*, A. Frenkel,* Yeshiva University*, J. Liu,* Arizona State University*, F. Tao*, University of Kansas

Partial oxidation of methanol to hydrogen and carbon dioxide offers a novel route in converting liquid fuel to hydrogen for fuel-cell systems and thus has been widely investigated in the past decade. One important category of heterogeneous catalysts for catalyzing this reaction is bimetallic nanoparticles which consist of continuous bimetallic sites in a metallic state. Isolation of such bimetallic sites through anchoring them on oxide could offer distinctly different catalytic performance in contrast to continuous sites on bimetallic nanoparticles.

Here we reported an isolated bimetallic site Pt_1Zn_n supported on ZnO which offers an extremely high catalytic activity with high selectivity for transformation of methanol to hydrogen with oxygen. It was prepared through a restructuring of singly dispersed Pt atoms on ZnO with reducing treatment. The formed isolated Pt atoms on ZnO was characterized with high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) along the projected [10-10] of ZnO as well as the corresponding structural model (Figure 1). The bright spots show single dispersion of Pt atoms. The offset of Pt atoms to the Zn atom row suggests Pt atoms are on the column of oxygen atoms, which indicates the bonding of Pt atom to Zn atoms. Photoemission feaures of Pt4f of the catalyst during catalysis were tracked with ambient pressure X-ray photoelectron spectroscopy (AP-XPS) using monochromated Al Kα (Figures 2). The resultant partial reduced state of Pt atoms under reaction conditions is consistent with the electronic state of Pt in Pt_1Zn_n bimetallic site.

Catalytic performance of the formed isolated Pt_1Zn_n bimetallic site in partial oxidation of methanol was evaluated and compared with Pt-Zn bimetallic nanoparticle catalyst (Figure 3). Isolated Pt_1Zn_n bimetallic site catalyst exhibits much higher activity per active site and selectivity to H_2 than Pt-Zn nanoparticle catalyst in transformation of methanol to hydrogen through partial oxidation. The cationic nature of these isolated bimetallic site in contrast to the metallic nature of active sites on a nanoparticle could be responsible for the differences in catalytic performance. This study illustrates that isoaltion of continuous bimetallic sites on a nonmetallic support is a new opportunity to tune catalytic performance of bimetallic catalysts.

5:00pm **IS+AS+SA+SS-MoA9 New Developments in Small Spot and Imaging Near Ambient Pressure XPS**, ***Andreas Thissen***, SPECS Surface Nano Analysis GmbH

Over the last 15 years, Near Ambient Pressure (NAP-) XPS has demonstrated its promising potential in a wide variety of applications. Starting from the Catalysis and Ice paradigm, the focus has shifted towards solid-liquid interfaces, liquid jets and in-situ electrochemistry. Initially, the experiments had to be carried out using advanced synchrotron sources to reach reasonable count rates. But now, the SPECS PHOIBOS 150 NAP offers optimized transmission for electrons, even at pressures up to and above 100mbar, so researchers can now use it with conventional X-ray and UV sources in their own laboratories. Because of the widened application fields, standard XPS is now also attainable when combined with easily adjustable monochromated X-ray sources that offer stable operation, small excitations spots, and high photon flux densities, even in Near Ambient Pressure conditions. The latest designs and results are presented showing small spot performance for spot sizes < 30 µm, while also showcasing the latest implementations of imaging NAP-XPS that uses a new concept allowing for lateral resolved measurements without a compromise in count rate and usability. Highlighting on how sample environments (in situ cells for gases and liquids, electrochemical cells, gas inlets) and integration are both absolutely essential to obtain relevant results from well-defined samples, the presentation will demonstrate the use of NAP-XPS systems for high throughput-XPS measurements, as well as a variety of applications.

5:20pm **IS+AS+SA+SS-MoA10 In Situ Measurement of the Abundances and Temperatures of the Constituents of Semiconductor Manufacturing Plasmas via Terahertz Absorption Spectroscopy: Comparison with Theoretical Models**, ***Yaser Helal***, *C.F. Neese, F.C. De Lucia,* The Ohio State University*, A. Agarwal, B. Craver, P.R. Ewing, P.J. Stout, M.D. Armacost*, Applied Materials, Inc.

Plasmas used by the semiconductor manufacturing industry are similar in pressure, temperature, and electron density to those used for the laboratory study of astrophysical neutrals, ions, and radicals. Thus, methods developed over several decades in the submillimeter/terahertz spectral region are directly applicable. Important attributes of terahertz absorption spectroscopy are that it can provide from first principles, without need for calibration, absolute concentrations and temperatures. Furthermore, since there are no intrusive probes, terahertz observations do not impact or change the plasma under study. Such measurements provide details and insight into the interactions and reactions occurring within the plasma and their implications for semiconductor manufacturing processes. In this work, a continuous wave, 0.5 – 0.75 THz absorption spectrometer was developed and used to study the processes in a commercial inductively coupled plasma (ICP) etch chamber. Because of the relatively long wavelength of the terahertz radiation, diffraction is more serious than in the optical regime. As a result, an important part of this work was the development of optical strategies to couple this spectrometer to the plasma reactor using its existing viewports. Comparisons of the experimental results with predictions from equipment models for ICPs will also be presented for Ar/CF_4/CHF_3 with varying pressures, powers, and gas mixture ratios. Comparisons such as this provide a basis for validating and improving models, whose development is a complex and difficult science in itself. The results presented in this talk show that terahertz rotational spectroscopy can provide unique and easy to interpret information about manufacturing plasmas and is a useful development tool for process, theoretical and physical models, and the improvement of etch methods.

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 ($1/\lambda \sim 600\text{-}4000\ \text{cm}^{-1}$) 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 MoS_2**, ***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-MoS_2 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-MoS_2 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

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*** NSTD Student Award Finalist**

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.

[1] F. Keilmann, Hillenbrand R., Phil. Trans. R. Soc. Lond. A 362, 787 (2004)

[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)

Plasma Science and Technology
Room: 210B - Session PS+EM-MoA

Directed Self Assembly and Plasma Synthesis of Novel Materials
Moderator: Eric Joseph, IBM T.J. Watson Research Center

2:20pm **PS+EM-MoA1 Forward and Inverse Computational Tools for Directed Self-Assembly**, *G.H. Fredrickson*, ***Sean Paradiso***, University of California at Santa Barbara **INVITED**

This presentation will provide a tutorial on the physics of bulk block copolymer self-assembly, explaining how molecular parameters such as polymer architecture, composition, and molecular weight influence the size and symmetry of nanoscale domains. In thin films, additional variables such as surface and substrate interactions and substrate topology are important in "directing" the self-assembly and thereby achieving morphologies and features useful for pattern transfer in lithography. A powerful computational framework based on polymer field theory will be described that enables simulations to be conducted for a wide range of block copolymer formulations subject to arbitrary topological confinement ("grapho-epitaxy") or substrate chemical modulation ("chemo-epitaxy"). Our recent work at UCSB has involved computational studies of block copolymer directed self-assembly (DSA) in a variety of confining templates that can be produced using conventional lithography tools and targeting both line/space patterns and vertical interconnects (VIAs). The research aims to identify polymer architectures and compositions along with template geometries and surface treatments that lead to robust DSA structures. Beyond process windows for perfect structures, we have studied defect states and the free energy landscape connecting them to perfect states, thereby providing estimates of equilibrium defect populations and kinetic barriers for defect annealing. I will finish the presentation with an example of an "inverse design" calculation, namely the identification of a template and polymer composition that optimally produces a desired self-assembled pattern. Further developments in this area will be necessary for DSA to become a practical tool in next generation lithography.

3:00pm **PS+EM-MoA3 Improvement of Block Copolymer Masked Silicon Etch Profile using Neutral Beam**, ***Deokhyun Yun***, *J.W. Park, H.S. Kim, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

These days, bottom-up block copolymer (BCP) lithography is widely investigated as alternative patterning method for deep nanoscale device replacing conventional top-down photolithography. The most widely used BCP material is polystyrene (PS)/polymethyl methacrylate (PMMA) and, nanoscale PS mask features formed on the substrates after the direct self-assembly are easily damaged by the plasma processing. Previously, neutral beam etching has been used to etch semiconducting materials without surface charging and damaging by using a highly directional radical beam instead of conventional plasma assisted ion beam. In this study, the nano-structured silicon was fabricated for nano-devices such as optical devices and transistor devices using BCP as the mask and the effect of Cl_2/Ar neutral beam instead of Cl_2/Ar ion beam on the etch characteristics of BCP and silicon was investigated. The use of neutral beam instead of ion beam decreased the degradation of BCP during the etching, therefore, more anisotropic silicon etch profile in addition to the improved etch selectivity of silicon over BCP could be observed. Also, by using the neutral beam instead of ion beam, the improvement of line edge roughness could be obtained.

3:20pm **PS+EM-MoA4 Plasma Etching of Directed Self Assembly based Patterns for Aggressively Scaled CMOS Applications**, ***Hiroyuki Miyazoe***, *H. Tsai, R.L. Bruce, S.U. Engelmann, M. Brink, A. Pyzyna,* IBM T.J. Watson Research Center, *C. Liu,* IBM Albany Nanotech Center, *A. Vora, D. Sanders,* IBM Almaden Research Center, *M. Maher, W. Durand, C. Ellison, G. Willson,* The University of Texas at Austin, *M. Guillorn, E.A. Joseph*, IBM T.J. Watson Research Center

As the feature size in CMOS technology continues to shrink, patterning below 30 nm pitch faces many challenges. Directed self-assembly (DSA) [1] and sidewall image transfer (SIT) [2] patterning techniques can augment conventional lithographic patterning by providing sublithographic multiplication of feature pitch. Recently, our group successfully demonstrated the electrical characterization of FinFET devices comprising fins formed by DSA of poly (styrene-block-methyl methacrylate) (PS-b-PMMA) block copolymers (BCPs) at 28nm fin pitch [3]. In addition, we demonstrated copper lines with dielectric patterns formed by DSA at 28nm pitch followed by metallization [4]. Patterning of Si, SiNx and SiOx at a ~24 nm feature pitch using PS-b-PMMA BCP was also shown [3]. In this work, we discuss a parametric study of factors impacting fine feature patterning to further optimize DSA line-space patterning using PS-PMMA BCPs at 28 and 24nm pitch, and high chi BCP at 20nm and 18.7nm pitch. The use of templated DSA to generate line-space structures in the aforementioned materials was used to investigate the control of critical dimension (CD), line edge roughness (LER) and line width roughness throughout the patterning process. The line roughness of the hardmask becomes smaller at the lower substrate temperature during etch. The CD of lines was controlled well between 11nm and 15nm at 28nm pitch by controlling the etching time while keeping the LER constant (at ~3nm). We also confirmed that O_2-free plasma gas chemistry is more advantageous for BCP patterning in case of organic-organic polymer. These initial patterning studies may play an important role in understanding feature formation and density limiting ground rules.

[1] J. Cheng et al., SPIE 2010, [2] H. Yaegashi. SPIE 2012, [3] Tsai, IEDM 2014, [4] Pyzyna VLSI 2015

4:00pm **PS+EM-MoA6 Microplasma Based Synthesis of Nanomaterials**, ***Michael Gordon***, University of California at Santa Barbara **INVITED**

We present a hybrid plasma spray deposition technique, based on geometrically-confined, supersonic microplasma jets, which can create a wide range of metal, metal oxide/sulfide, and semiconductor nanoparticles and nanostructured thin film materials (e.g., CuO/CuS, ZnO, SnO_2, NiO/$NiFe_2O_4$) on virtually any surface. Organometallic or aerosolized precursors are broken down in a hollow cathode microplasma jet under different reducing/oxidizing atmospheres at high pressure (10-100 torr), creating a directed flux of active metal and oxide species for the subsequent growth of nanostructured films. Interaction of the jet afterglow with the background gas can create additional species (e.g., excited neutrals, radicals, etc.) which participate in film growth. By adjusting supersonic flow characteristics and plasma operating conditions, deposits ranging from isolated nanoparticles to films of fibers, aggregates, nanowires, and dense columns can be realized. The talk will highlight our recent efforts in nanomaterial synthesis via microplasmas with emphasis on the physics of the jet source, dynamics of the growth process, and applications such as solar cell electrodes, photo(electro)catalysis, and nanogranular films for magnetic exchange bias applications.

4:40pm **PS+EM-MoA8 Nucleation of Silicon Nanocrystals in a Remote Plasma without Subsequent Coaguation**, ***Ilker Dogan***, Eindhoven University of Technology, Netherlands, *S.L. Weeks, S. Agarwal,* Colorado School of Mines, *M.C.M. van de Sanden*, Dutch Institute for Fundamental Energy Research (DIFFER), Netherlands

We report on the growth mechanism of spherical silicon nanocrystals (Si-NCs) in a remote expanding Ar plasma using a time-modulated SiH_4 gas injection in the microsecond time range. Under identical time-modulation parameters, we varied the local density of the SiH_4 gas by changing its stagnation pressure on the injection line over the range 0.1-2.0 bar. We observed that nanocrystals were synthesized in a size range from 2 nm to 50 nm with monocrystalline morphology. Smaller nanocrystals (2-6 nm) with narrower size distributions and with higher number densities were synthesized with an increase of the SiH_4 gas-phase density. We related this observation to the rapid depletion of the number density of the molecules, ions and radicals in the plasma during nanocrystal growth, which can primarily occur via nucleation with no significant subsequent coagulation. In addition, in our remote plasma environment, rapid cooling of the gas in the particle growth zone from 1500 K to 400 K significantly reduces the coalescence rate of the nanoparticles, which makes the coagulation process highly unlikely. Our observations on nanocrystal formation via nucleation indicated that subsequent coagulation for further growth is not always an essential step on nanoparticle formation.

5:00pm **PS+EM-MoA9 Atmospheric Plasma Synthesis of Metallic Platinum Nanoparticles for PEMFC Technology using an Organometallic-Carbon Solution Nebulized in the Post-Discharge of an RF Torch**, ***Joffrey Baneton***, *D. Merche,* ULB, Belgium, *M. Raes,* VUB, Belgium, *V. Debaille,* ULB, Belgium, *G. Caldarella, V. Stergiopoulos,* ULg, Belgium, *H. Terryn,* VUB, Belgium, *N. Job,* ULg, Belgium, *F.A.B. Reniers*, ULB, Belgium

Catalytic layers are one of the most important components of proton exchange membrane fuel cells (PEMFC) because they directly influence the transport of matter and the reactivity of the electrodes [1]. In many cases, platinum associated with carbon black forms the most interesting material because of its very high catalytic activity [2]. Unfortunately, some limitations remain due to the cost of platinum and the difficulty to control the structure of the carbon support.

In this study, we propose a new promising technique using platinum (II) acetylacetonate [$Pt(acac)_2$] powder mixed with porous carbon and nebulized in a RF atmospheric plasma torch directly on commercial gas diffusion layer (GDL). This fast and "one-pot" methodology leads to the formation of homogeneous and reproducible samples with a variable and controlled content of metallic platinum on the surface, as analyzed by X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM). The catalytic activity per mass unit can be studied by a combination of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and electrochemical measurements.

We demonstrate that the plasma treatment and mostly the reactive oxygen species play a critical role in the activation of the support surface and the binding of the platinum nanoparticles on it, reinforcing previous observations [3,4]. In the case of an argon-oxygen plasma pretreatment of the GDL, a significant increase of the platinum content on the surface can be observed.

The influence of different process parameters on the synthesis of the platinum nanoparticles was studied. We show that the carrier gas flow rate, the power injected in the discharge and the treatment time do not have a significant impact on the surface composition. On the other hand, some nebulizer parameters such as the number of pulses or the loading of Pt-C allow the tuning of the amount of Pt grafted on the surface without altering its metallic nature.

Finally, the influence of the type of carbon powder (e.g. CB, CX or CNTs) was investigated. It appears that it can modify the surface organization and consequently also the intrinsic characteristics of the material. It reveals that the distribution of platinum nanoparticles and the access to the catalytic sites can be optimized depending of the porosity and the active surface of the carbon support.

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5:20pm **PS+EM-MoA10 Low Energy Helium Ion Irradiation Induced Surface Modification of Metals**, ***Irem Tanyeli****, FOM Institute DIFFER, Netherlands, *L. Marot, D. Mathys,* University of Basel, Switzerland, *M.C.M. van de Sanden,* FOM Institute DIFFER, Netherlands, *G. De Temmerman*, ITER Organization

Many applications, such as energy harvesting, energy storage, optoelectronics, demand nanomaterials and/or nanostructured surfaces for an enhanced activity. Various techniques, which can be grouped under top-down and bottom-up approaches, exist and are worked on by many researchers in order to fulfill the demands of these applications. There are some critical requirements that needs to be satisfied by nanostructures before being implemented in any application, such as high porosity, good contact between different crystallites and good electrical conductivity. Standard nanostructuring approaches, such as wet-chemical processing, can give very homogeneous particle sizes, but the contact between the particles is often poor and a necking treatment is needed to alleviate this limitation. In this study, Helium ion induced nanostructuring is proposed as an efficient technique. This top-down approach provides a good control over morphology, high porosity, good conductivity and it enables post processing, such as oxidation and nitridation.

Metal surfaces are exposed to pure Helium plasma under extreme ion flux (in the range of 10^{23} $m^{-2}s^{-1}$) and low ion energy (< 100 eV) conditions at Pilot-PSI, linear plasma generator. Different surface modifications on various metals, such as iron, titanium, copper and aluminum, are observed.[1] Pillar like structures are formed on copper and aluminum surfaces, whereas fiber like nanostructures are observed on iron surface. Controlled nanostructure formation on tungsten and molybdenum surfaces has been reported.[2] Consistently, nanostructure formation on iron surface has been controlled with surface temperature and ion fluence in this study.[3] It has been known that metal oxides are good candidates to be used as photoelectrodes in photoelectrochemical cells. WO_3 and α-Fe_2O_3 are two of the most widely studied photoanodes. Hence, Helium ion induced tungsten and iron nanostructured surfaces are oxidized to the desired phases to be tested in photoelectrochemical cells. 1mA/cm^2 of photocurrent density for WO_3 has been achieved.[4]

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Plasma Science and Technology
Room: 210A - Session PS-MoA

Plasma Diagnostics, Sensors and Control I
Moderator: Erik Johnson, LPICM-CNRS, Ecole Polytechnique, France, Jeffrey Shearer, IBM Research Division, Albany, NY

2:20pm **PS-MoA1 Submillimeter Studies of Molecular Plasmas: Applications to Semiconductor Plasma Processing**, ***Frank De Lucia***, Ohio State University **INVITED**

The use of submillimeter (smm) absorption spectroscopy to study molecular plasmas is well established. This has been driven by a number of applications including the molecular astrophysics of free radicals and ions, diagnostics of excitation and energy transfer in laser plasmas, and fundamental physical chemistry.

Attributes of smm spectroscopy of plasmas include: (1) They are transparent and essentially noise free in the smm, (2) Very high resolution leads to essentially 'absolute' specificity and low clutter backgrounds, (3) It is a non-invasive probe with straightforward sampling, (4) Calibration free measurement of absolute concentrations can be obtained from first

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*** Coburn & Winters Student Award Finalist**

principles, (5) The spectra provide measurements of the rotational/translational temperatures, (6) The technique can probe 'dark' chambers, and (7) Measurements can be 'real time.

Limitations include: (1) The molecules require a dipole moment, (2) The technique is more challenging as pressure is raised above 1 Torr, and (3) Because of diffraction, it requires a larger probe beam.

In this talk we will first discuss the basic physics and chemistry that underlies the smm spectroscopy of low-pressure plasmas. We will then describe results initially obtained on a test reactor at OSU provided by Applied Materials, followed by results obtained on production and research reactors at Applied Materials. This will include measurements of concentrations and temperatures of plasma constituents as a function input flows, discharge power, and time.

3:00pm **PS-MoA3 Using Broadband Absorption Spectroscopy to Elucidate Energy Partitioning and its Impact on Surface Reactivity**

Joshua Blechle, *A.R. Hanna, E.R. Fisher*, Colorado State University

The partitioning of energy within plasma systems is of vital importance to plasma chemistry as it provides insight into reactivity via possible species formation and decomposition mechanisms as well as its significant contribution to surface reactivity of individual plasma species. Here, such investigations are used to determine the internal and kinetic energies of species within a variety of inductively coupled plasma systems. To obtain this information, broadband absorption spectroscopy (BAS) and the imaging of radicals interacting with surfaces (IRIS) technique were utilized to determine species energetics (vibrational, rotational, and translational temperatures). In particular, the vibrational and rotational temperatures of NO, N_2, OH, and O_2 in various gas mixtures are measured, indicating significantly higher vibrational temperatures (i.e. >3000K) than rotational temperatures (i.e. <1000K) are obtained. One focus of this work is the development of a BAS system and the impact of various methods of data collection on determined temperatures evaluated using different computational models. These data are also used to demonstrate the relationship between internal energetic and observed surface scatter coefficients (S) for NO, OH, and other plasma species, which is directly related to surface reactivity (R). Such observations allow for unique insight into these plasma systems and the integral role energy partitioning plays in the assessment and understanding of complex plasma chemistry.

3:20pm **PS-MoA4 CF_3^+ Fragmentation by Electron Impact Ionization of Perfluoro-Vinyl-Ethers**

Yusuke Kondo, *K. Ishikawa, T. Hayashi, Y. Miyawaki, K. Takeda, H. Kondo, M. Sekine, M. Hori*, Nagoya University, Japan

In plasma etching processes, the densities of chemically reactive species have attracted attention. A higher etch yield for SiO_2 at lower ion impact energies was reported when using CF_3^+ ions.[1] Perfluoro-vinyl-ether forming selectively CF_3^+ ions were reported.[2] Here we extensively studied in details the gas phase fragmentations of perfluoro-vinyl-ether.

A quadrupole mass spectrometer (QMS; Hiden Analytical, EQP) was installed in the chamber wall of the commercial plasma etching reactor. PPVE (CF_3-CF_2-CF_2-O-CF=CF_2, $C_5F_{10}O$) or PMVE (CF_3-O-CF=CF_2, C_3F_6O) was introduced into the chamber and maintained at a pressure of 1.0 Pa.

Dissociative ionization caused by impact with 20 eV electrons provided positive ion fragmentation pattern to three peaks for PMVE: CF_3^+, $C_2F_2O^+$ and $C_3F_6O^+$, and five peaks for PPVE: CF_3^+, $C_2F_2O^+$, $C_2F_5^+$, $C_3F_7^+$ and $C_5F_{10}O^+$. Figure 1 shows comparison of the ion efficiency for CF_3^+ between (a) PPVE and (b) an isomer of PMVE. The large ionization efficiency of CF_3^+ was experimentally observed significantly as the leading cause of large cross-sections for dissociative ionization of CF_3^+ ions. For comparison, the CF_3^+ ion density fragmented from perfluoro-alkanes is only 30 to 40%. By the energetic electron impact on the perfluoro-vinyl-ethers, excess energy is distributed among internal energies at the vinyl-ether bond, due to polarization of the charge on the bridging oxygen atom. The fragmentation via direct bond rupture into smaller product ions occurs more favorably than the rearrangement or cleavage into molecules with large mass.

[1] K. Karahashi *et al.* J. Vac. Sci. Technol. A **22** 1166 (2004). [2] M. Nagai *et al.*, Jpn. J. Appl. Phys. **45** 7100 (2006); Y. Morikawa *et al.*, Jpn. J. Appl. Phys., **42**, 1429 (2003).

3:40pm **PS-MoA5 A Comprehensive Quantitative Study of Low Pressure Inductively-Coupled Plasmas in Cl_2, O_2 and Mixtures**

M. Foucher, D. Marinov, P. Chabert, LPP-CNRS, Ecole Polytechnique, France*, A. Agarwal, S. Rauf,* Applied Materials Inc., ***Jean-Paul Booth***, LPP-CNRS, Ecole Polytechnique, France

Inductively-coupled plasmas in diatomic electronegative gases such as Cl_2 and O_2 are widely used in semi-conductor fabrication for gate etching and photo-resist stripping. Moreover they are an archetype for plasmas in simple electronegative gases with the advantage that techniques exist to measure the densities of nearly all their stable and reactive species. They provide an opportunity to benchmark models such as the Hybrid Plasma Equipment Model. We are then undertaking a comprehensive set of measurements in the pure gases and their mixtures.

The plasma is sustained in a cylindrical chamber (55 cm diameter,10 cm height) by a 4-turn planar coil excited at 13.56 MHz above a dielectric window. Pure gases (Cl_2 and O_2) were studied over a range of pressure [5-80 mTorr] and RF power [50-550 W]. The effect of O_2 addition (0-100%) to Cl_2 plasmas was studied at 10 mTorr 500W. The electron density was determined by hairpin resonator probe. The Cl and O atom absolute densities and surface reaction coefficients were obtained by Two-Photon Absorption Laser-Induced Fluorescence. A novel ultra-broadband high sensitivity absorption bench was used to measure ground state and vibrationally excited Cl_2 and vibrationally excited O_2, as well as OCl, OClO and Cl^- ions.

In all gas mixtures, the electron density was observed to increase initially with gas pressure, pass through a maximum and then decrease at higher pressure. In O_2 a broad maximum is observed around 40 mTorr, whereas for Cl_2 the electron density peaks at 10 mTorr before dropping sharply. This difference can be attributed to rapid dissociative attachment of electrons in the case of Cl_2. In all cases the electron density increases with RF power. In O_2, highly vibrationally excited molecules $O_2(v)$ were observed (with v up to 18), and analysis of the rotational structure of the O_2 Schumann-Runge bands showed rotational temperatures (=translational temperatures) ranging from 400 K (10mTorr 100W) to 900 K (80 mTorr 500W). The non-equilibrium vibrational distribution may be attributed to electron impact excitation combined with low rates of V-T energy transfer processes in O_2. In contrast, in pure Cl_2 the vibrational temperature is equal to the gas translational temperature, (~1000K) due to efficient V-T transfers between Cl_2 and Cl atoms. In Cl_2/O_2 mixtures the densities of electrons and Cl and O atoms all decreased when O_2 or Cl_2 is added to the pure gas (Cl_2 or O_2). This coincides with the formation of ClO and OClO, which consumes the atoms which are easier to ionize than molecules.

We are currently working on modeling of these results to obtain a deeper understanding of the kinetics of Cl_2/O_2 plasmas.

4:00pm **PS-MoA6 Optical Emission Diagnostics for Detection of High Energy Electrons in Argon Plasmas**

Shicong Wang, *J. Boffard, C.C. Lin, A.E. Wendt*, University of Wisconsin - Madison

The electron energy distribution function (EEDF) is one of the most important and fundamental parameters in low temperature plasmas. The high-energy range of the EEDF in particular is responsible for ionization, excitation and gas phase chemistry, which are critical for many industrial applications. Non-invasive OES diagnostics provide an attractive means to measure EEDFs, using emissions from argon states excited by electron collisions [1,2]. Emission lines dominated by excitation of ground state argon atoms are particularly sensitive to the population of high energy (>13 eV) electrons. We report on optical emission diagnostics for detection of energetic electrons in argon plasmas. The OES diagnostic makes use of an emission model based on measured argon excitation cross sections that computes the relative emission intensities at a selected set of wavelengths, with a trial EEDF as input. The trial EEDF that produces the best fit to the spectrum measured in the experiment is determined after a search in which the shape and average energy of the trial EEDF is varied. In both pulsed argon inductively coupled plasmas (ICPs) and capacitively coupled plasmas (CCPs), a high electron temperature has been previously observed at the beginning of the pulse period in time-resolved OES measurements. Meanwhile, the relative argon emission intensities between emissions originating from upper levels populated primarily by high energy and low energy electrons , respectively, (i.e., 420.07/419.83 nm line ratio) imply the existence of a `hot tail' of energetic electrons, as compared to a Maxwellian distribution. In addition, the OES method of detecting high energy electrons is explored in the presence of a supplemental source of energetic electrons. A biased auxiliary set of heated filaments will be used to inject high energy electrons into an argon inductively coupled plasma. The filament bias voltage will be varied to control the energy of emitted electrons, and the filament heater current will be controlled separately to vary the emitted electron flux. The OES diagnostic is used to observe the changes in emission spectra and extracted EEDF caused by the supplemental energetic electrons. The OES method will be examined and compared to Langmuir probe measurements of EEDF as the energy and current of the supplemental electron population are systematically varied.

The authors acknowledge support from NSF grant PHY-1068670.

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[2] Boffard et al., Plasma Sources Sci. Tech. 19 (2010) 065001.

4:20pm **PS-MoA7 Plasma Characteristics in a Dual-Frequency Inductively Coupled Plasma Source for the Etch Tool**, ***Vladimir Nagorny***, Mattson Technology, *V. Godyak*, RF Plasma Consulting

It is always desirable to have more than one antenna in ICP plasma source for etch for better both radial uniformity control and process window. So, configurations with two antennas are being used in ICP for quite a while. However, there is always a question about their interference.

Recently Mattson Technology introduced an etch tool with a dual frequency ICP plasma source [1]. The logic behind complementing a standard 13.56MHz antenna with a 2MHz antenna with ferrite core was quite simple - no interference between antennas, high efficiency 2MHz design [1–3] of the second antenna and respectively low additional cost. This source demonstrated large operating window, high plasma stability in both electro-positive and electro-negative gases, good process control. With this source design it is possible to tune process uniformity (Max-Min) down to 1% and better on a blanket wafer.

Energizing plasma with different frequencies put a reasonable question, if the two essentially different frequencies create similar processing plasmas comparing to a 13.56MHz drive or not. To answer this question, a comprehensive study of the electron energy probability functions, EEPF have been measured in Ar and in real processing plasmas, including gas mixtures that generate depositing plasma. The measurements performed in a wide range of processing condition with different power ratio at 13.56 and 2 MHz have demonstrated independence of the measured EEDFs on frequency, but only on the total absorbed power, gas composition and its pressure. These results are in agreement with earlier observation in different reactors [4] and with analysis of ionization and electron energy balances in gas discharge plasma [5].

[1] V. Nagorny, D. Lee and A. Kadavanich, *US PTO Publication* US20140197136, *patent pending*

[2] V.A. Godyak, *US Patent* 8920600.

[3] V.A. Godyak, C. Crapuchette, V. Nagorny, *US PTO Publication patent pending.*

[4] N. Hershkowitz, J. Ding, R.A. Breun, R.T.S. Chen, J. Mayer, and A.K. Quick 1996 *Phys.Plasmas* **3** 2197

[5] V.A. Godyak 2006 *IEEE Trans. Plasma Sci.* **34** 755

4:40pm **PS-MoA8 Spatial Oscillations and Frequency Shifts in Pulsed Capacitively Coupled Plasmas**, ***John Poulose***, *L.J. Overzet,* The University of Texas at Dallas, *S. Shannon,* North Carolina State University, *D. Coumou,* MKS Instruments, *M.J. Goeckner*, The University of Texas at Dallas

Pulsed plasma provides a method to 'independently' control ion and neutral fluxes. Temporal and spatial evolutions of the pulsed plasmas have been studied to provide a better understanding of transitory behavior in such systems. The optical emission intensities (OEIs) of various spectral lines from pulsed plasmas through Ar, O_2, N_2, CF_4 gases and $CF_4/O_2/Ar$ gas mixtures have been collected. The OEIs measured from $CF_4/O_2/Ar$ gas mixtures show an axial oscillation of intensity with an approximate speed of 10^6 cm per second. This oscillation starts at the plasma strike and dampens to the background during the first 10 µs in 1 kHz pulse frequencies or lower. Radio frequency voltage and current measurements show changes over similar time periods. The transient reactance has been observed to correspond to the sheath formation in the OEI studies. Measured current and voltage frequencies have been observed to shift/pull by as much as 400 kHz during the initial turn on phase. The amount of the frequency pull is dependent on gas composition, electrode gap, pressure, and pulse properties. This shift occurs as a reaction to the plasma formation, specifically, the sheath development. We will present these results and the effects of other parameters on the transitory behavior of pulsed discharges.

5:00pm **PS-MoA9 Curling Probe Measurement of Electron Density in Pulse-Modulated Plasma at High Frequency**, ***Anil Pandey***, Chubu University, Japan, *W. Sakakibara,* DOWA Thermotech, Japan, *H. Matsuoka,* DOWA Thermotech, *K. Nakamura, H. Sugai*, Chubu University, Japan

*Curling prob*e (CP), a modified form of microwave resonator probe has recently been proposed [1] which enables the local electron density measurement even in reactive plasma for non-conducting film deposition. The electron density is obtained from a shift of ¼ wavelength-resonance frequency of the spiral slot antenna in discharge ON and OFF monitored by a network analyzer (NWA). CP is a compact monitoring tool (minimum diameter 6 mm) coated with alumina or yttria for applications to semiconductor plasma processing. A variant of CP installed with an optical fiber, called *opto-curling probe* (OCP) has also been developed which enables simultaneous monitoring of electron density and optical emissions from plasma [2]. In this paper we demonstrate that CP can be applied not only to a constant density plasma but also to a plasma pulse-modulated at high frequency such as several tens of kHz. In case of pulse-modulated discharge, synchronization of discharge pulse with frequency sweep of NWA must be established [3]. Such CP measurement was performed in a pulsed glow discharge plasma primarily used for metal-nitridation. A CP of 16-mm diameter was inserted in a cylindrical chamber of 60 cm in diameter and 50 cm in length. A negative high-voltage pulse of -1.0 to -2.0 kV was applied to a cathode, which generates a pulsed glow plasma in different discharge gas at varying pressures. The pulse frequency was changed from 0.4 to 25 kHz with various duty cycle ratios. The NWA (Agilent E5071C) was externally triggered using *on point* mode and the electron density in glow phase and afterglow phase was measured in time-resolved manner in argon, nitrogen and hydrogen discharges. At higher pulse frequencies (>5 kHz), the electron density was found to be time-modulated and didn't decay completely to zero. Also, a minimum time resolution of 2 µs was attained. Thus, CP is concluded to be a powerful tool for the time-resolved electron density monitoring in pulse-modulated plasma often used in industrial materials processing.

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[2] A. Pandey, K. Nakamura, and H. Sugai, Appl. Phys. Express 6, 056202 (2013).

[3] A. Pandey, W. Sakakibara, H. Matsuoka, K. Nakamura, and H. Sugai, Appl. Phys. Lett. 104 (2014) 024111.

5:20pm **PS-MoA10 Detection of Biomedically Relevant Reactive Oxygen Species in Atmospheric Pressure Plasmas**, ***Sandra Schröter****, *J. Bredin, K. Niemi, J.P. Dedrick,* University of York, UK, *M. Foucher,* Ecole Polytechnique, France, *N. de Oliveira, D. Joyeux, L. Nahon,* Synchrotron Soleil, France, *J.-P. Booth,* Ecole Polytechnique, France, *E. Wagenaars, T. Gans, D. O'Connell*, University of York, UK

Cold atmospheric pressure plasmas (APP) are known to be sources for reactive oxygen species (ROS) [1,2], which makes them potentially well suited for biomedical applications. Examples of ROS of interest are atomic oxygen (O) and hydroxyl radicals (OH) because of their high reactivity and as potential precursors for longer lived reactive species. In order for APPs to achieve widespread usage in therapeutic applications, controlled production of the species of interest and hence their quantification is essential. However, at atmospheric pressure this is particularly challenging due to the short lifetimes of excited states as a result of their rapid de-excitation by collision induced quenching. Additionally, determination of the exact gas composition in APPs is difficult, especially in the jet region, where a gradual transition from the feed gas to the ambient air occurs.

In order to overcome these challenges, we will present three advanced diagnostic techniques used to quantify absolute densities of reactive species in helium RF APPJs with molecular admixtures, namely picosecond Two-photon Absorption Laser Induced Fluorescence (ps-TALIF) [3], high-resolution Fourier-transform synchrotron VUV absorption [4,5] and UV-Broad-Band Absorption Spectroscopy (UV-BBAS). Under a variation of the water content in the gas phase, absolute densities of OH and O were determined in the plasma core to be in the order of 10^{20} m^{-3} and 10^{19} m^{-3} respectively. The densities were found to increase with increasing water admixture. Additional insight was gained about the air diffusion into the plasma effluent by mapping the lifetimes of the excited atomic oxygen in the axial and radial directions. Typical lifetimes in the order of a few nanoseconds were decreasing away from the nozzle and radial centre of the plasma jet due to diffusion of air from the ambient environment into the jet region.

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*** Coburn & Winters Student Award Finalist**

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic
Room: 112 - Session SA-MoA

New Insights in Correlated Materials, Organic Materials and 2D Solids
Moderator: Herrmann Dürr, Stanford University, Petra Rudolf, University of Groningen

2:20pm **SA-MoA1 Operando Soft X-ray Spectromicroscopy on Electronic States of Graphene Transistors**, ***Hirokazu Fukidome***, Tohoku University, Japan

Graphene, the tiny monolayer honeycomb, is promising for high-speed communication owing to excellent electronic properties, such as carrier mobility and saturation velocity, arising from a linear band dispersion, and vanishment of short-channel effects owing to ultrathinness of graphene. The ultrathinness, on the other hand, deteoriates device performances because the ultrathinness easily induces interface modulation of electronic properties of the graphene channel in the graphene transistor. This produces a gap between material properties of graphene layers and device performances of graphene transistor.

To bridge the gap, we have developed operando observation, i.e. observation under operation (gate-bias application in this work), of electronic states using soft x-ray spectromicroscopies with spatial resolutions of 20-100 nm, such as photoemission electron microscopy (PEEM) [1] and three-dimensional scanning photoelectron microscopy (3D nano-ESCA) [2]. This operando PEEM reveals gate-bias-dependent modulation of electronic states of the lateral interface between the graphene channel and contact metal. This interface modulation is brought about by the charge transfer between the graphene channel and the metal contact in the lateral direction. The charge transfer region is relatively large owing to a limited density of states near the Dirac point of graphene. In addition, the operando 3D nano-ESCA directly evidences the linear band dispersion of the graphene transistor in operation by doing a pinpoint C 1s core-level spectromicroscopy at the center of graphene channel, followed by analyzing the shift of the graphene peak by the gate bias.

In conclusion, these operando spectroscopies provides valuable information on graphene transistors. Further operando spectromicroscopy study is in progress to clarify the reason for degradation of high-frequency performances of the graphene transistor [3].

Profs. Oshima, Horiba and Kotsugi and Dr. Nagamura and staff members of BL17SU and BL07LSU of SPrinb-8 are gratefully appreciated for the operando spectromicroscopy. This work has been done partly as the projects of BL07LSU and BL17SU at SPring-8 and also as the academic-industry alliance NEDO project.

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2:40pm **SA-MoA2 Micro-metric Electronic Patterning of a Topological Band Structure using a Photon Beam**, ***Nick de Jong***, *E. Frantzeskakis, B. Zwartsenberg, Y. Huang, B.V. Tran, P. Pronk, E. van Heumen, D. Wu, Y. Pan,* University of Amsterdam, *M. Radovic,* Paul Scherrer Institute, *N.C. Plumb, N. Xu,* Paul Scherrer Institut*, M. Shi,* Paul Scherrer Institute*, A. de Visser, M.S. Golden*, University of Amsterdam

We discuss a method of "writing" spatial micro-metric patterns in the electronic surface band structure of the topological insulator (TI) $Bi_{1.46}Sb_{0.54}Te_{1.7}Se_{1.3}$. Due to fine-tuning of the bulk stoichiometry this material is truly insulating, making it a promising candidate for applications where the special transport properties of the topological protected surfaces states are necessary. However despite the insulating character bulk in transport experiments, the spectroscopic fingerprint of $Bi_{1.46}Sb_{0.54}Te_{1.7}Se_{1.3}$ is not that of an insulator. Due to band bending, the conduction band is partly occupied at the surface of the material. We present a way to counteract the occupation of the conduction band in both global and local spatial scales. Namely, we make use of an extreme ultra violet photon beam with superband gap energy and a flux exceeding 10^{21} photons/(s m^2) as a "writing tool". This is a three-step process. First an area of approximately 500 mm x 500 mm is mapped out by angle resolved photoemission spectroscopy (ARPES), taking a spectrum of the topological surface state at each sample location. Secondly, we expose selected sample locations to a higher fluence photon beam. These locations form a pre-defined pattern. Finally, the first map of the area is then again by ARPES. In this way we are able to shift the electronic surface band structure and drive the bulk conduction band to the unoccupied part of the spectrum. This shift is observed to be very local and in our case is only limited by the size of the beam and not by the approach itself.

3:00pm **SA-MoA3 Switching 2D Materials Properties with Light**, ***Alessandra Lanzara***, University of California, Berkeley **INVITED**

Understanding how superconductivity emerges from other competing phases and how this balance evolves through the phase diagram is one of the biggest challenges in the field of high Tc superconductors. By using high resolution time- and angle- resolved photoemission spectroscopy (tr-ARPES) we are able to directly probe the effects of optical excitation on the electronic structure of cuprate superconductors, and study the resulting quasiparticles, superconducting gap, and Cooper pair formation dynamics near their natural time- scales. Direct measurements of these and other non-equilibrium spectral phenomena through the phase diagram further illustrate the power of this unique time- and momentum-resolved spectroscopy. These results reveal new windows into the nature of the pairing interaction in high Tc superconductors.

3:40pm **SA-MoA5 Science-driven Requirements for Soft X-ray Free Electron Lasers**, ***Fulvio Parmigiani***, Elettra-Sincrotrone Trieste, Italy **INVITED**

Starting from the archetypal FERMI externally seeded FEL, recent theoretical and experimental progress has shown the possibility of producing fully coherent, variable polarization and tunable, soft-X-ray, ultra-short pulses at high repetition rate. This ultimate achievement will unlock the gate for performing X-ray-based experiments that are qualitatively different from those available at any current or planned X-ray source. Here we will review the experiments and the ideas that represent the science frontier in soft X-ray, time-resolved spectroscopy, coherent imaging and scattering experiments. These studies will lead to an understanding of fundamental dynamics, occurring on the ultrafast time and nanometer spatial scales, needed for addressing a broad range of science essential for resolving our complex and long-term energy challenges, environmentally urgent questions and demanding problems in bioscience and novel materials.

4:20pm **SA-MoA7 Revealing Spin Texture Dynamics in Complex Materials via Time-resolved Resonant Soft X-ray Scattering**, ***Robert Schoenlein***, Lawrence Berkeley National Laboratory **INVITED**

Self-organized mesoscale spin textures emerge in complex materials due to coupling between charge, spin, and lattice degrees of freedom, and play a significant role in establishing the exotic properties of these materials. Here we focus on two examples: (1) topologically-protected spin vortices (Skyrmions) in the insulating multiferroic Cu_2OSeO_3 which result from a combination of symmetric spin-exchange interactions, and antisymmetric exchange resulting from a Dzyaloshinskii-Moriya (DM) interaction, and (2) helical spin states in the lanthanide metal Dy which result from competition between spin-orbit coupling, magneto-elastic effects, and long-range exchange coupling mediated by the indirect RKKY interaction.

A key scientific challenge is to understand the origin of these ordered spin textures, and the fundamental mechanisms and time-scales for manipulating these phases, in order to develop a knowledge base for potential technology applications. Resonant X-ray scattering (RXS) is a powerful direct probe of charge, spin, and orbital ordering in complex materials. Current synchrotron X-ray sources and new X-ray free-electron lasers enable RXS to be applied in the time domain. This provides an important new route to disentangle the cause-effect interactions that drive the formation and evolution of spin textures in complex materials.

Optical pump and resonant X-ray scattering studies of the skyrmion phase in Cu_2OSeO_3 reveal six-fold symmetric magnetic peaks that appear as satellites around the (001) Bragg peak. Transient optical excitation at 2.3 eV (above band gap) suppresses the spin ordering on a ~40 ps time scale – significantly faster than from excitation below gap at 1.5 eV, indicating an electronically-driven collapse of the skyrmion phase. We will discuss the fluence dependence of the conical and skyrmion phases and the motion of the ordering wavevector in response to excitation above and below the insulating gap.

We also report on recent studies of an epitaxially grown Y/Dy/Y multilayer film to understand the dynamics of the core-level spin helix in response to excitation of the conduction electrons responsible for the exchange interactions. Ultrafast optical excitation at 1.5 eV results in ultrafast injection of unpolarized spins into the 500 nm Dy film via nonequilibrium diffusion. The subsequent dynamics of the helical phase, revealed by time-resolved resonant X-ray scattering, differ significantly from those observed in ferromagnetic materials due to the relationship between the core spins and conduction electron Fermi surface nesting.

5:00pm **SA-MoA9 Electronic States of Functional Molecular Materials Probed by Low-energy Excitation**, ***Satoshi Kera***, Institute for Molecular Science, Japan **INVITED**

Understanding the impacts of electron-phonon coupling as well as weak intermolecular interaction on the electronic state is required to discuss the mechanism of charge transport in functional molecular materials. Ultraviolet photoelectron spectroscopy (UPS) is known to be a powerful technique to study the electronic states. However, the experimental study of fine features in the highest occupied molecular orbital (HOMO) state has not been progressed till recently due to difficulty in the sample preparation, damages upon irradiation and so on, though it can offer a variety of key information, that is essential to comprehend charge-hopping transport and small-polaron related transport in the ordered monolayer film [1] as well as to coherent band transport in the molecular single crystal [2,3]. We present recent findings regarding on the precise measurements of electronic states for large aromatic organic molecular materials by using low-energy excitation UPS.

Use of low-energy excitation realizes unique experiments to find out the followings as an advantageous for the organic materials; i) low-kinetic energy of photoelectron may achieve resonance excitation channel to open eyes for many events accessed, e.g. on a degree of electron cloud localization, inelastic scattering phenomena at the interfaces and a breaking the sudden approximation, and ii) high-photoionization cross section and bulk-sensitive probe may detect a quasi-particle state in very narrow HOMO band. Combining all findings above mentioned, characteristics of an electron in the functional molecular material has been embossed.

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[2] N. Ueno et al., Prog. Surf. Sci. 83 (2008) 490.

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Advanced Surface Engineering
Room: 212A - Session SE+EM+EN-MoA

Thin Film Technologies for Energy Storage, Conversion and Harvesting

Moderator: Michael Stueber, Karlsruhe Institute of Technology, Andrey Voevodin, Air Force Research Laboratory

2:20pm **SE+EM+EN-MoA1 Properties of Zinc Oxide Thin Films Grown on Silicon Wafers by Pulsed Laser Deposition**, ***Yilu Li***, *J.W. Wrobel, M.K. Michael*, University of Missouri-Kansas City

Pulsed ultraviolet light from a XeF excimer laser was used to grow thin films of zinc oxide on (111) p-type silicon wafers within a versatile high vacuum laser deposition system. Pressure, target temperature and distance from the target to the substrate can be adjusted in the system. Scanning electron microscopy, energy dispersive X-ray spectroscopy, X-ray diffraction spectroscopy and ellipsometry had been used to analyze the structures and properties of ZnO thin film products.

3:00pm **SE+EM+EN-MoA3 Synthesis of Crystallized and Nanostructured TiO_2 Thin Films by Reactive Magnetron Sputtering for Application as Photoanode in Dye Sensitive Solar Cells**, *J. Dervaux, P.-A. Cormier, S. Konstantinidis,* Université de Mons, Belgium*, P. Moskovkin, S. Lucas,* University of Namur, Belgium, ***Rony Snyders***, Université de Mons, Belgium

Nowadays, the efficient use of renewable energies, and more specifically of solar energy, represents a major economic and environmental issue. Among the potential solutions, the Dye Sensitive Solar Cells (DSSC) present many advantages. In order to improve the efficiency of DSSC, TiO_2 nanoparticles, which are usually used as photo-anode, could be replaced by nanostructured TiO_2 thin films. Indeed, a photo-anode of ordered porous nano-columnar TiO_2 would provide large surface area for dye absorption, fast electron transfer path, enhanced light trapping, and tight interfaces to conducting electrodes and contributes to a high fill factor and an overall higher cell efficiency. In view of this application, the anatase phase of TiO_2 is usually the preferred polymorph as electron acceptors in DSSCs even if a synergistic effect exists between anatase and rutile with an optimal rutile content of around 13 wt%.

In this work, nanostructured and crystallized TiO_2 thin films are synthesized by reactive magnetron sputtering combined with Glancing Angle Deposition (GLAD). The substrate temperature, the substrate bias voltage and the rotation speed were varied in order to determine the best experimental conditions leading to (nano-)porous films with anatase TiO_2 columns. The chemical composition, the crystalline structure and the microstructure of the films were analyzed by XPS, XRD, SEM and TEM, respectively while the surface area is evaluated by the BET method.

It is demonstrated that many type of microstructures (tilted columns, straight pillars, chevrons,…) are obtained by combining the GLAD parameters and the sputtering conditions. On the other hand, depending on these growth conditions, the phase constitution can be tuned from amorphous to pure rutile or anatase phases including mixtures of both polymorphs. The surface area of the synthesized layer strongly depends on the experimental conditions and on the associated microstructure. The highest obtained value is of ~ 140 m^2/g for a tilted columnar amorphous/anatase sample which is significantly better than the values reported for TiO_2 nanoparticules systems (~ 60 m^2/g). On the other hand, a clear correlation between the surface area and the dye absorption is demonstrated revealing a good impregnation of the layer. It is also demonstrated that this impregnation behaviour is depending on the size of the dye molecule revealing different populations of pores as a function of their size. This is supported by TEM and modelling data using NASCAM, a 2D-3D Kinetic Monte Carlo code for the simulation of deposition, diffusion, nucleation and growth of films on a surface.

3:20pm **SE+EM+EN-MoA4 Silver-Carbon-Nanotube Metal Matrix Composites for Metal Contacts on Space Photovoltaic Cells**, ***Omar K. Abudayyeh***, *C. Nelson, S.M. Han,* University of New Mexico*, N. Gapp, D.M. Wilt*, Air Force Research Laboratory

The advanced solar cells used in space vehicles today are rapidly moving towards thin-film-based inverted metamorphic multijunction (IMM) solar cells mounted on flexible substrates. However, the IMM cells are more prone to cracking than state-of-the-art triple junction cells. The cell cracking can lead to metal contact failure on IMM cells, compromising the power generation. To mitigate the power loss and increase the lifetime of IMM cells, silver metal films imbedded with carbon nanotubes (CNTs), otherwise known as metal matrix composites, have been developed and investigated for the reinforced mechanical strength against stress-induced cracking. We have primarily focused on (1) surface functionalization of CNTs to make their surface more hydrophilic and wetting to metals, (2) optimization of a cyanide-free electrochemical deposition of silver, (3) electrochemical deposition, drop casting and nanospreader technique to control the composite microstructure, and (4) mechanical and electrical characterization of the composite films. We observe that carboxylation of CNTs produces a stable, homogeneous suspension of negatively charged CNTs at pH > 6. Lustrous-mirror-finish silver films are also successfully deposited, using a commercial cyanide-free silver-plating solution with precise control of current density. Currently, one of the microstructures being explored is a silver-carbon-nanotube layer-by-layer structure, where the surface coverage of CNTs is an important parameter that directly affects the CNT packing fraction and metal intercalation through the CNT network. We quantify the CNT surface coverage as a function of different deposition variables by digitally analyzing scanning electron microscopy images. In this presentation, we will further discuss how this surface coverage correlates to the mechanical and electrical properties of the MMC films. We characterize the mechanical properties, using nanoindentation and strain failure tests. The initial nanoindentation analysis reveals that the composite film has a lower elastic modulus (10 GPa) than pure silver (73 GPa) or CNT (1000 GPa). The lower elastic modulus is attributed to the electroplating process of silver, in which hydrogen is incorporated and trapped within the composite. Our finite element analysis also corroborates this speculation, where the elastic modulus near 10 GPa is predicted with approximately 4% void fraction. While the composite elastic modulus is lower than that of pure silver, the strain failure tests show that carbon nanotubes can bridge 20 to 50-mm-wide microcracks, maintaining electrical conductivity of the composite.

3:40pm **SE+EM+EN-MoA5 Laser Liftoff of Single Crystal GaAs Thin Films and Energy Conversion Devices**, ***Bruce Clemens***, *G. Hayes, V. Parameshwaran, A. Jan, J.B. Reeves*, Stanford University **INVITED**

GaAs and related III-V sphalerite materials offer a wide array of tunable characteristics that lend themselves to many advanced device technologies. However, the cost of GaAs substrates limits their use, specially for photovoltaics. Separating epitaxially-grown layers from a growth substrate can reduce costs, however the current approach, which uses an acid to laterally etch an epitaxial sacrificial layer, is slow and can damage other device layers. Here, we demonstrate laser lift-off as a new approach that is orders of magnitude faster, and that enables more freedom in the selection of other device layers. We grow a structure with a spatially-tuned optical absorption coefficient by growing a small-band-gap, pseudomorphic layer between the GaAs substrate and a GaAs film and device structure. By using InGaAsN with a band gap of 0.9 eV for this layer, we achieve high absorption of 1064 nm (1.17 eV) light from a Nd:YAG nanosecond laser pulse, while GaAs is essentially transparent for this wavelength. Illumination through the back of the GaAs substrate with laser fluences of about 0.7 J/cm^2 achieves transfer of the GaAs layer to a flexible polymer substrate. Transmission electron microscopy and x-ray diffraction show that the initial InGaAsN layer is coherently strained to match the GaAs substrate, and that the GaAs film is strain-free and free of dislocations, both before and after lift-off. Thermal modeling shows only modest heating outside of the InGaAsN layer, so that the film or device above the InGaAsN layer experiences minimum thermal exposure. Examination of the lift-off interfaces shows evidence of melting and re-solidification. We demonstrate a process using additional InGaP etch layers that allow for quick and easy clean-up of this melted region, resulting in restoration of the original GaAs wafer surface to a condition suitable for re-use. Thus our process can transform the GaAs substrate from a consumable to a manufacturing tool. Device performance and material properties of lifted-off devices will be reported.

4:20pm **SE+EM+EN-MoA7 Optical and Structural Properties of Metal-dielectric Composite Films**, ***Lirong Sun***, *N.R. Murphy, J.G. Jones, J.T. Grant*, Air Force Research Laboratory

In this work, the metal - metal oxide composite films were prepared in multilayer stacks. A medium layer of silver or a mixture of silver and oxide (SiO_2, Al_2O_3, ZnO and ITO) was embedded between the host (SiO_2, Al_2O_3, ZnO and ITO) materials. The mixture of silver and oxide was deposited by co-sputtering the silver target and one oxide target in pure argon simultaneously using DC and pulse DC magnetron sputtering techniques. The optical constant of composite films was tailored by varying deposition time of the medium layer, deposition conditions and host material. The absorbing spectral peaks were influenced by silver content, silver particle sizes and oxide matrix. The *in situ* spectroscopic ellipsometry data was performed in real time during film growth to derive film thickness and optical constants. The dispersion results were further correlated with absorption spectra, film density, grain sizes and surface morphology by UV-Vis-NIR spectra, X-ray diffraction, X-ray reflectivity and scanning electron microscope measurements.

5:00pm **SE+EM+EN-MoA9 Atomic Layer Deposition of Alumina and Titania Passivation Layers in Microchannel Reactors for Coke Suppression**, ***Hao Feng***, Xi'an Modern Chemistry Research Institute, China

Alumina and titania thin films are deposited inside the channels of stainless steel tubes by atomic layer deposition to deactivate the metal surface for the purpose of coke suppression. The ALD equipment is modified to incorporate the high-aspect-ratio metal tubes into the flow path. Experiment parameters are adjusted to ensure complete and uniform coverage of the internal surface areas of the metal tubes. The thicknesses of the passivation layers are precisely controlled by adjusting the number of ALD cycles. In coking experiments the passivated metal tubes are used as reactors for thermal cracking of a hydrocarbon fuel composed of C_{12}-C_{16} paraffins. The lifetime of the experiment system passivated by ALD alumina films can be up to 5 times longer compared to the system using bare metal tubes as the reactor. By analyzing the tested metal tube samples it is discovered that the ALD alumina film remains intact after the coking experiment so that the metal catalyzed filament coke formation can be completely inhibited by the alumina passivation layer. The anti-coking performances of ALD titania passivation layers are also noticeable but not as stable. The formation of filament cokes can also be suppressed by titania passivation layers. However, the ALD titania films tend to crack during the coking experiments. This could lead to failures of the passivation layers and acceleration of coke formation.

Surface Science
Room: 113 - Session SS-MoA

Organics and Ionic Liquids: Surfaces, Layers, Interfaces and Chirality

Moderator: Janice Reutt-Robey, University of Maryland, College Park, John Russell, Jr., Naval Research Laboratory

2:20pm **SS-MoA1 ZnTPP, PTCDA, TCNQ, and TTF on TiO2(110): Molecule-Oxide Interaction and Electronic Energy Level Alignment**, ***Charles Ruggieri***, *S. Rangan, R.A. Bartynski,* Rutgers, the State University of New Jersey, *J.I. Martinez,* Institute of Materials Science of Madrid, Spain, *F. Flores, J. Ortega*, Autonomous University of Madrid, Spain

The injection of charge between transition metal oxides and organic materials depends crucially on the interface barrier that is determined by the organic electronegativity, the possible space charge layer formed in the oxide, and the chemical interaction between the oxide and the organic. We investigate the interfaces of TiO2(110) and four organic molecules, ZnTPP, PTCDA, TCNQ, and TTF, representing a broad range of electronegativities, and the electronic energy level alignment for each interface, using a combination of direct and inverse photoemission spectroscopies and theoretical modelling. In particular, we analyze contributions to the electronic energy level alignment from oxide-molecule chemical hybridization, induced electrostatic dipoles due to molecular distortion, and charge transfer, and the relative importance of these phenomena to each case. In this way, we provide a detailed description of the wide range of interactions influencing the final electronic energy level alignment for weakly and strongly interacting organic on TiO2 (110).

2:40pm **SS-MoA2 Characterizing the Influence of Water on Charging and Layering at Electrified Ionic-Liquid/Solid Interfaces**, ***Hsiu-Wei Cheng***, Max-Planck-Institut für Eisenforschung GmbH, Germany, *P. Stock,* Max-Planck Institut für Eisenforschung GmbH, Germany, *B. Moeremans,* Universiteit Hasselt, Belgium, *T. Bamipos,* Max Planck Institut fur Eisenforschung GmbH, Germany, *X. Banquy,* University of Montreal, Canada, *F.U. Renner,* Universiteit Hasselt, Belgium, *M. Valtiner*, Max-Planck Institut für Eisenforschung GmbH, Germany

The importance of water on molecular ion structuring and charging mechanism of solid interfaces in room temperature ionic liquid (RTIL) is unclear and has been largely ignored. Water may alter structures, charging characteristics and hence performance at electrified solid/RTIL interfaces utilized in various fields including energy storage and conversion or catalysis. Here, we utilize Atomic Force Microscopy to directly measure how water alters the interfacial structuring and charging characteristics of [C_2mim][Tf_2N] on mica and electrified gold surfaces. On hydrophilic and ionophobic mica surfaces, water-saturated RTILs induce strong ion layering by dissolution of surface-bound cations and a resulting high surface charging. In contrast, layering of dry RTIL at uncharged mica surfaces is weakly structured. At electrified, hydrophobic and ionophilic gold electrodes, significant water effects were found only at positive applied electrochemical potentials. Here, the influence of water is limited to interactions within the RTIL layers, and is not related to a direct electrosorption of water on the polarized electrode. More generally, our results suggest that effects of water on interfacial structuring of RTIL strongly depend on both (1) surface charging mechanism, and (2) interfacial wetting properties. This may greatly impact utilization and design of RTILs and surfaces for interface dominated processes.

3:00pm **SS-MoA3 Interfaces of Ionic Liquids**, ***Hans-Peter Steinrück***, Universität Erlangen-Nürnberg, Germany **INVITED**

Ionic liquids (ILs), salts with melting points below 100 °C, represent a fascinating class of liquid materials, typically characterized by an extremely low vapour pressure. Besides their application as new solvents or as electrolytes for electrochemical purposes, ILs are also used in catalysis. Two important concepts in this context are Supported Ionic Liquid Phase (SILP) and Solid Catalyst with Ionic Liquid Layer (SCILL). In both, a high surface area solid substrate is covered with a thin IL film, which contains either a homogeneously dissolved transition metal complex for SILP, or which modifies catalytically active surface sites at the support for SCILL. Thereby, the interfaces of the IL with the gas phase and with catalytic nanoparticles and/or support materials are of critical importance. It has recently been demonstrated that these interfaces and also the bulk of ILs can be investigated in great detail using surface science studies in an ultrahigh vacuum environment. From angle-resolved X-ray photoelectron spectroscopy, detailed information on the surface and bulk composition of non-functionalized and functionalized ILs, on segregation and enrichment effects, on the dissolution and reactivity of catalytically active metal complexes in ILs, on the growth of ultrathin IL-layers, and even on liquid phase reactions studied in situ in the IL, can be derived. Various examples will be discussed.

H.-P. Steinrück and P. Wasserscheid, *Ionic Liquids in Catalysis*, Catal. Lett. **2015**, 145, 380.

H.-P. Steinrück, *Recent developments in the study of ionic liquid interfaces using X-ray photoelectron spectroscopy and potential future directions*, Phys. Chem. Chem. Phys. **2012**, 14, 2510.

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F. Maier, J. M. Gottfried, J. Rossa, D. Gerhard, P. S. Schulz, W. Schwieger, P. Wasserscheid, H.-P. Steinrück, *Surface enrichment and depletion effects of ions dissolved in an ionic liquid. An X-ray photoelectron spectroscopy study*, Angew. Chem. Int. Ed. **2006**, 45, 7778.

3:40pm **SS-MoA5 Free-Standing Gold Nanoparticles on Ultrathin Ionic Liquid Films Studies by Low Energy Ion Scattering (LEIS) Analysis**

__Thomas Grehl__, P. Bruener, ION-TOF GmbH, Germany*, L. Calabria, P. Migrowski, D.L. Baptista, F. Bernardi,* Laboratory of Molecular Catalysis, UFRGS, Brazil*, H. Brongersma,* ION-TOF GmbH, Germany*, J. Dupont*, Laboratory of Molecular Catalysis, UFRGS, Brazil

Metal nanoparticles (NPs) in ultrathin films have a variety of applications nano-optical and nano-electronic devices. Several methods have been developed in order to synthesize such films. However, those methods result in "capped" NPs, instead of free-standing NPs which would be a more versatile alternative precursor for ultrathin film growth.

Ionic liquids are known to facilitate well-defined formation of Au NPs from sputter deposition and self-organization of the particles close to the surface [1]. The size and potential shape of the NPs can be tailored by the properties of the ionic liquids. Applying this principle of NP formation to ultrathin films of ionic liquids is a promising route by which to easily form free-standing NPs in a well controlled manner.

In this study we analyze silicon wafer supported ultrathin films of both hydrophilic and hydrophobic imidazolium based ionic liquids forming an "ionic carpet like" structure. This structure is decorated with gold NPs having a size of 5 - 10 nm from the application of sputter deposition of gold onto the ionic liquid. A range of analytical techniques is applied to the samples, including XPS, XRD, AFM and electron microscopy. Here we present primarily the results from high resolution and high sensitivity Low Energy Ion Scattering (LEIS).

LEIS is the most surface sensitive technique for the elemental characterization of the outermost atomic layer. Noble gas ions having a kinetic energy of a few keV are scattered from the individual surface atoms. By measuring the energy loss in the scattering event, the mass of the respective surface atom can be determined, while the intensity of the scattering signal is proportional to the surface coverage. LEIS has been successfully applied to ionic liquids by several groups to elucidate the termination of the liquid. In addition the LEIS data contain information on the composition of the first few nm of the sample. The latter is used to determine the thickness of the self-organized layer of NPs and allows the thickness measurement of any film covering the gold.

The gold nanoparticles are deposited by sputtering into the hydrophobic (AMI.NTf2) and hydrophilic (AMI.BF4) ionic liquids on Si(111) for 5 and 10 s. The LEIS spectra show gold signal for the hydrophobic ionic liquid. Apparently the gold NPs are out of the probed range of the LEIS technique (10 nm). In contrast to that, the LEIS spectra of the hydrophilic ionic liquid after gold deposition show the presence of gold below the surface. The mean thickness of the organic layers covering the NPs is 6 nm (5 s deposition) and 4.3 nm (10 s deposition).

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4:00pm **SS-MoA6 Early-Stage Solid-Electrolyte Interphase (SEI) Formation: Probing Molecular Carbonate Decomposition Pathways and Artificial Lithium Ethylene Dicarbonate Monolayers**

***Wentao Song**, J.E. Reutt-Robey*, University of Maryland, College Park

The Solid Electrolyte Interphase (SEI) formed at the Li-ion battery (LIB) anode plays a major role in battery cycle life and safety. The ethylene carbonate (EC) electrolyte is known to undergo reduction to a mixture of lithium salts at the onset of SEI formation, but the product branching and sensitivity to electrode structure have not been determined. We report the use of temperature programmed desorption (TPD) and reaction spectroscopy (TPRS) to quantify interactions between the molecular carbonates, ethylene carbonate (EC) and dimethyl carbonate (DMC), and model Li- C(0001) anode surfaces prepared in situ. Both EC and DMC interact weakly with the clean C(0001) surface with adsorption energies of 0.60 ± 0.06 and 0.64 ± 0.05 eV, respectively. Submetallic lithiation of C(0001) significantly increases the binding energies of molecular carbonates, and the range of measured values indicates EC solvation of lithium ions. In the presence of metallic lithium, 1.5 monolayers of EC undergoes complete decomposition, resulting in 70.% organolithium products and 30% inorganic lithium product. Further structural analysis of the early stage organolithium salt, lithium ethylene dicarbonate (LEDC), was performed with UHV-STM. A pulsed microaerosol molecular beam source permitted controlled deposition of LEDC (from dimethyl formamide solvent) on Ag(111). Elongated LEDC monolayer islands spontaneously form in three distinct 120 degree rotational domains, all aligned with the close-packed silver direction. Further deposition increases island size and density, with little change in island shape. Molecularly resolved STM images reveal a LEDC monolayer structure with a 1.1874 ± 0.0079 nm x 0.5793 ±0.0055 nm unit cell containing one LEDC. A structural model is presented that accounts for the anisotropy of the LEDC islands. The O-Li-O linkages in the structural model define the long-axis (fast growth direction) of the islands. The LEDC islands are thermally stable up to at least 80°C, and can be imaged over days under UHV. Preliminary STS measurements (performed in Z-V mode) are consistent with significant differences in the local density of electronic states for LEDC islands relative to the Ag(111) substrate.

4:20pm **SS-MoA7 Racemization and Enantioselectivity on Metal Surfaces**

Georg Held, University of Reading, UK **INVITED**

The last decade has seen a dramatic increase in research into chiral surface systems, driven by the growing demand for optically pure chemicals in drug manufacturing and, hence, a desire for enantioselective heterogeneous catalysts. These avoid the problem of phase separation inherent in homogeneous enantioselective processes which are predominantly used today. So far, significant success has been achieved by modifying achiral surfaces with chiral molecules thus creating stereo-selective reaction environments [1,2]. Alternatively, intrinsically chiral metal and mineral surfaces show enantioselective behavior without such modifiers [3,4], although these mechanisms are much less well understood. In our work we use synchrotron-based spectrocopies, such as XPS and NEXAFS, alongside LEED and temperature-programmed desorption to characterize the thermal stability, bond coordination and orientation of chiral probe molecules on achiral and intrinsically chiral model catalyst surfaces. The talk will present examples of adsorption systems on both types of surfaces. Particular emphasis is on small chiral amino acids (e.g. alanine, serine), which show razemization as well as enantioselectivity at several levels depending on the substrate and the length of the side-chain of the molecule [5-8].

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5:00pm **SS-MoA9 Mapping of Enantioselective Reaction Kinetics across Surface Structure Space: Tartaric and Aspartic Acid on Cu(111) Structure Spread Single Crystals**

***Andrew Gellman**, A. Reinicker*, Carnegie Mellon University

On single crystal metal surfaces, enantioselectivity is, perhaps, the most subtle form of structure sensitive surface chemistry. Enantioselectivity can be observed on naturally chiral metal surfaces with structures that are traditionally described as having flat low Miller index terraces separated by kinked step edges, thereby lacking mirror symmetry. This work has mapped the enantiospecific decomposition kinetics of tartaric acid (TA) and aspartic acid (Asp) on 225 different single crystal planes exposed by the surface of a Cu(111) Surface Structure Spread Single Crystal (S^{4}C). The Cu(111) S^{4}C is a single crystal polished into a spherical dome shape that exposes a continuous distribution of surface orientations vicinal to the Cu(111) plane. During isothermal decomposition, XPS has been used to map the temporal evolution of the coverages of TA and Asp at points across the Cu(111) S^{4}C. On Cu surfaces, both TA and Asp decompose by an explosive, vacancy-mediated decomposition mechanism consisting of an initiation step and a vacancy-mediated explosion step. The rate law for this process is parameterized by an initiation rate constant, k_i, and an explosion rate constant, k_e. Under isothermal conditions, the measured extent of reaction versus time at each point on the S^{4}C has been used to fit the decomposition rate law and estimate the values of k_i, and k_e as functions of local surface structure across the Cu(111) S^{4}C. These maps reveal that k_i is maximum on surfaces with high densities of the close packed (100) steps and minimum on surfaces with high densities of the close packed (110) steps. As the angle between the surface and the (111) plane increases, k_i increases linearly with step density. Along the direction containing the surfaces with (100) steps, the initiation step dominates and the kinetics look first-order. Along the directions exposing (110) steps the kinetics are dominated by the explosion step. In the case of Asp decomposition on the Cu(111) S^{4}C, the decomposition kinetics are also sensitive to the chirality of the local surface orientation. Collectively, these data provide the deepest insight yet obtained in to the structure sensitivity of surface explosion reactions and the structural origins of enantioselectivity on naturally chiral surfaces.

5:20pm **SS-MoA10 Enantioselective Adsorption on Platinum Surfaces**

S. Karakalos, __Francisco Zaera__, University of California

Enantioselectivity in the adsorption of chiral compounds on solid surfaces may lead to preferential crystallization, a possible route to chiral separation of racemic mixtures, and also to a way to design enantioselective catalytic chemical reactions. Tests on the uptake of simple molecules on metal single-crystal surfaces as a function of the enantiocomposition of the adsorbate has revealed several interesting kinetic and thermodynamics. Specifically, we have been exploring possible enantiospecific behavior during the uptake of propylene oxide (PO) on Pt(111) surfaces. Three related observations will be reported here. In the first set of experiments, the amplification of enantioselectivity during adsorption was demonstrated for the case of a surface seeded with a small amount of enantiopure PO and then dosed with propylene, a non-chiral molecule, as the amplifier. Chiral chemical titration and isothermal kinetic adsorption experiments using collimated effusive molecular beams indicated the possibility of reaching enantioselectivity excesses of over 60% this way. Monte Carlo simulations provided a kinetic explanation for this effect in terms of both an adsorbate-assisted adsorption process and a bias in the chiral configuration the propylene molecules are driven to upon adsorption on the surface. The second example refers to the uptake of PO itself, where lower saturation coverages are seen with the racemic mixtures versus enantiopure samples by approximately 20%. This behavior could be explained in terms of adsorbate-assisted adsorption with different probabilities for homo- versus hetero-enantiomeric pairs. Finally, it was determined that the enantiomeric composition of PO monolayers eventually reverses the direction of the enantiospecfic enrichment seen in the kinetic uptake.

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.

Vacuum Technology
Room: 230B - Session VT-MoA

Extreme High Vacuum
Moderator: Martin Wüest, INFICON Ltd., Liechtenstein, Jay Hendricks, NIST

2:20pm **VT-MoA1 An XHV Standard: Making Absolute Measurements in the UHV and XHV**, ***James A. Fedchak****, J. Scherschligt, M.S. Sefa*, National Institute of Standards and Technology (NIST)

Ultra-high vacuum (UHV) and extreme-high vacuum (XHV) underpins much of the manufacturing and research found in today's high-tech products and advanced research programs. Several National Metrology Institutes have high-vacuum standards that allow the calibration of vacuum gauges and mass spectrometers down to 10^{-8} torr, but few have capabilities to perform absolute calibrations in the UHV and below. To date, most vacuum standards utilize the dynamic expansion technique. Low vacuum pressure is realized by scaling down a known high pressure to a low pressure region via an orifice with well-characterized dimensions . Although these standards are often described as being "primary", these standards are not, in fact, either primary or fundamental. Here, we describe NIST's efforts to build a UHV/XHV standard covering the pressure range from 10^{-8} torr to 10^{-12} torr. We will pose and propose and answer to the question: Is it possible to build an absolute vacuum sensor that is also a primary standard in the UHV and XHV?

2:40pm **VT-MoA2 Reducing the Ultimate Pressure of Turbo Pumps for XHV Applications**, ***Julia Scherschligt****, J. Fedchak, M.S. Sefa*, NIST

Typically NEG or ion pumps are used to achieve XHV pressures, but these are unsuitable for our application because they're gas specific. Turbo pumps can pump all gases, but the ultimate pressure for a common turbo pump is dominated by outgassing and is in the range of about 10^{-10} torr. We investigate reducing the ultimate pressure of a turbo pump for XHV applications.

3:00pm **VT-MoA3 XHV Cryopump Performance and Limitations for the Jefferson Lab Polarized Electron Source**, ***Marcy Stutzman****, P.A. Adderley, M. Poelker*, Thomas Jefferson National Accelerator Facility

Cryopumps are typically limited to pressures above 1x10^-10 Torr. This is partly due to the lower pump speeds for hydrogen and other light gasses that dominate systems approaching XHV. Additionally, the cryosorbers and adhesives in cryopumps are typically not compatible with the bakeouts of systems used to reduce water vapor pressure in XHV systems. A series of investigations will be described using a commercial XHV cryopump from Leybold, both alone and with the NEG and ion pumps typically used in the Jefferson Lab electron source. The benefits and limitations of using this cryopump for our applications will be examined.

3:20pm **VT-MoA4 A Comparison of Reduced Outgassing Rates for Air-Baked and Vacuum-Baked Stainless Steel Vacuum Chambers**, ***Makfir Sefa***, *J. Fedchak, J. Scherschligt*, National Institute of Standards and Technology (NIST)

Stainless steel is the most common metal used in the construction for ultrahigh vacuum (UHV) and extremely high vacuum (XHV) chambers. Hydrogen outgassing from the chamber walls is the predominant residual gas and it limits the lowest attainable pressure level in vacuum systems. There are several methods for reducing hydrogen outgassing rates from stainless steel chamber walls. High temperature ($T > 400$ °C) heat treatments are typically used to remove hydrogen from the bulk material and reduce outgassing. In this work, a comparison of reduced outgassing rates for high temperature air-baked and vacuum-baked stainless steel chambers is presented. We also will describe a simple apparatus that allowed us to directly compere outgassing rates from two different heat treatment methods.

4:00pm **VT-MoA6 Deposition of Non-Evaporative Getters (NEG) in Very Narrow Chambers**, ***Andre Anders***, *X. Zhou, Y. Yang, C. Swenson*, Lawrence Berkeley National Laboratory

Several next-generation accelerators require much narrower beam pipes than in the past in order to gain better control of beam position and shape. For example, diffraction-limited synchrotrons currently under construction or in the design phase call for vacuum chambers as narrow as 4 mm at certain sections. For such narrow chambers, the vacuum conductance is greatly reduced making it difficult to reach the ultrahigh vacuum requirements that are customarily required for accelerators. The solution seems clear: the beam pipes and other vacuum components have to be the pump. Non-evaporative getters (NEG) coatings are the straight-forward answer to these challenges. In this contribution we report about progress to coat very narrow vacuum chambers with NEG coatings using pulsed sputtering techniques at relatively high process gas pressures. We discuss deposition rates, film composition, various issues encountered and initial tests of pumping performance.

This work was supported by the Laboratory Directed Research and Development Program of Lawrence Berkeley National Laboratory under U.S. Department of Energy Contract No. DE-AC02-05CH11231.

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 NV^0 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.

[1] R. Igarashi, et al, Nano Lett. 2012, **12**, 5726

[2] A. Hegyi, E. Yablonovitch, Nano Lett. 2013,**13**, 1173

[3] R. Chapman, T. Plakkhoitnik, Opt. Lett. 2013, **38**, 1847

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 bi-layer 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 spectroscopic 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 MoS_2 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√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.

Atom Probe Tomography Focus Topic
Room: 211D - Session AP+AS-TuM

New Applications of Atom Probe Tomography
Moderator: Arun Devaraj, Pacific Northwest National Laboratory

8:00am **AP+AS-TuM1 Development of Atom Probe Tomography for Studying Nuclear Corrosion Issues**, ***Daniel Schreiber***, Pacific Northwest National Laboratory **INVITED**

Material degradation and corrosion create significant challenges to nuclear energy production, both in terms of the structural integrity of plant components and also in the long-term disposal of high-level radioactive waste. For structural materials, stress corrosion cracking (SCC) continues to be a prominent issue for Ni-base alloys in the high temperature (~320 °C in pressurized water reactors) corrosive reactor environment. Despite decades of research, there has yet to be a consensus on the fundamental mechanisms that control SCC response. On the other hand, the long-term disposition of high-level nuclear waste generated by nuclear energy production continues to be an open question. Vitrification of high-level waste into a relatively stable form (e.g. borosilicate glass) is being actively pursued. However, disagreement exists about the long-term stability of the glass if/when exposed to ground water in a geologic repository due to an ill-defined rate-limiting process controlling glass dissolution. In both cases, high-resolution microscopy techniques including atom probe tomography (APT) provide unique opportunities to test various mechanistic theories with unprecedented spatial resolution and chemical sensitivity. Such studies have only recently been made possible through the advancement of site-specific focused ion beam (FIB) sample preparation methods and pulsed-laser APT systems, creating a unique environment for revolutionary discoveries.

In this talk, I will discuss the development of APT methods for characterizing SCC microstructures in select model and commercial alloys and also for characterizing the dissolution of model vitrified nuclear waste glasses. The corrosion of metals and the dissolution of glass present unique but overlapping challenges in sample preparation, data acquisition and data interpretation that will be discussed in detail. Highlights will be presented in both cases on how APT is changing the way we view the fundamental mechanisms dictating SCC of metals and glass alteration.

8:40am **AP+AS-TuM3 Using Aqueous Solutions by Cryo-Fixation As a Matrix for Analyzing Materials in APT**, ***Stephan Gerstl***, *B. Scherrer,* ETH Zürich, Switzerland, *J.M. Cairney,* University of Sydney, Australia, *R. Spolenak, R. Wepf*, ETH Zürich, Switzerland **INVITED**

Atom probe tomography has progressively engaged the world of materials characterization with 3-dimensional nanometer-level maps of various dense materials. These atom maps have been the attraction of the technique because they enable new perspectives and analysis of solid materials literally atom by atom. The analysis of soft organic materials, even aqueous solutions, has however been a long-standing issue as it is impaired by contamination, uncertain phase formation, and questionable observed states. These outcomes have been interrogated, retested, and re-analyzed to better understand the artifacts involved. Here we present the development steps achieved together with the APT results obtained of three aqueous based solutions: a water-based citrate solution, a 1:1 water-ethanol mixture, and a commercially available marginally alcoholic beverage. These aqueous solutions were chosen so as to exhibit differences in their mass-spectrum response due to their dissimilarities. The methodologies enabling these analyses require arresting the liquids so they are stable in vacuum environments, sharpening them to a needle geometry, and transporting them between chambers whilst not altering their structural integrity; all steps being done close to LN_2 temperatures. The main challenge was with contamination, which needs to be minimized and separated from the material of interest in the analysis. The cryo-fixation method involves plunge freezing the region of interest (ROI) in cryogenic liquids, sharpening the ROI in a FIB fitted with a cryogenically cooled stage, and field evaporating it in a retrofitted cryo-transfer enabled LEAP 4000X-HR.

All aqueous specimens could be analyzed successfully; with the resulting amounts of ROI analyzed being small (only a thin film is probed due to sample geometry), trends and fluctuations in ion concentrations have been interrogated and will be presented.

The application space of this technique will be considered in terms of using fluids as matrices and designing the experiments to increase the volume of soft materials analyzed.

11:00am **AP+AS-TuM10 Atom Probe Tomography Investigation of TiSiN Thin Films Made Possible by ^{15}N Isotopic Substitution**, ***David Engberg***, Linköping University, Sweden, *L.J.S. Johnson,* Sandvik Coromant, Sweden, *M.P. Johansson-Jöesaar,* SECO Tools AB, Sweden, *M. Odén,* Linköping University, Sweden, *M. Thuvander,* Chalmers University of Technology, Sweden, *L. Hultman*, Linköping University, Sweden

TiSiN is one of the most important materials for commercial wear resistant coatings on cutting tools. Understanding of the growth and structure of these coatings has become increasingly important for optimizing their performance. Yet knowledge regarding the solid solubility, distribution, and stoichiometry of SiN_y has been lacking in the complex metastable TiN-SiN structure. Atom probe tomography (APT) in combination with analytical electron microscopy provides a way to attain compositional information in 3D on the nanometer scale. However, mass spectrum overlaps of N and Si ions have so far prevented such APT analyses. By growing TiSiN coatings with ^{15}N using cathodic arc deposition, we show that the mass spectrum overlaps of Si and N can be largely avoided. $TiSi^{15}N$ films of two compositions, $Ti_{0.81}Si_{0.19}{}^{15}N$ and $Ti_{0.92}Si_{0.08}{}^{15}N$ in a predominantly cubic structure, have been studied using APT. We find evidence of Si-Si clustering on the nanometer scale, while there are no indications of overstoichiometric SiN_y $(y \approx 1)$.

11:20am **AP+AS-TuM11 Investigating the Alternating Cation/Anion Compositions in a High-Voltage Li-Mn-Rich Oxide Electrode during First Charge-Discharge Cycle using Atom Probe tomography**, ***Baishakhi Mazumder***, *D. Mohanty, C. Daniel, D. Wood III*, Oak Ridge National Laboratory

High-voltage layered lithium and manganese-rich (LMR) oxides are potential cathodes for high-energy-density lithium-ion batteries for electric vehicles1. Unfortunately, structural transformation during charging and discharging in these oxides2 leads to undesired phenomena, such as voltage fade during subsequent cycles and lower columbic efficiency in the first cycle, that remain stumbling blocks for practical usage. Understanding the micro-structural changes during the first cycle is critical to obtaining fundamental insight regarding the activation mechanism(s) related to the first cycle capacity loss. In this work, Atom Probe Tomography (APT) has been employed to obtain the 3D microstructural and sub-nm-level compositional information of LMR oxides during the first cycle to resolve the activation mechanism(s) that lead to structural transformation.

The greatest challenge for APT analysis from the actual electrode materials is the complexity in creating needle-shaped specimens. Owing to the discontinuous geometry of the electrode, which is characterized by non-uniform interconnected channels, it is extremely difficult to make a structurally stable needle for controlled field evaporation. Micro-fractures and irregular evaporation due to differences in evaporation fields between the composite elements during APT analysis is also challenging. Additionally, experimental parameters, including tip temperature, laser energy, and detection rate, all strongly impact the field-evaporation and subsequent data analysis. By overcoming these challenges, reliable and reproducible data has been obtained after optimizing the experimental parameters and developing a reliable procedure to prepare stable samples. Mass spectra reveal molecular complexes MxOy for M=Ni,Mn,Co, while the Li appears predominantly as elemental ions. The 3D distributions as well as the compositions of each element were obtained for each sample at different states of charge during the first cycle. These data provides insight towards understanding the structural rearrangements during the first charge-discharge cycle that correlates with the first cycle irreversible capacity loss.

1) M.M. Thackeray, et al., J. Mat. Chem.17 3112 (2007)

2) D. Mohanty, et al., Chem. Mat. 26 6272 (2014)

Research supported by CNMS, which is a DOE Office of Science User Facility.LMR material was obtained from Argonne National Laboratory. The electrodes/cell fabrication, and cell testing were carried out at the DOE's Battery Manufacturing R&D Facility at Oak Ridge National Laboratory, which is supported by VTO within the core funding of the ABR subprogram. Authors thank Dr. Jianlin Li at ORNL for fabricating electrodes.

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.

Electronic Materials and Processing
Room: 210E - Session EM-TuM

Beyond CMOS: Materials and Devices for a Post CMOS Era

Moderator: Christopher Hinkle, University of Texas at Dallas, Suzanne Mohney, Penn State University

8:00am **EM-TuM1 Secret Ingredients in Thin-TFET: A 2D Material-based Transistor**, ***Grace Huili Xing***, Cornell University **INVITED**

Thin-TFET stands for Two-dimensional Heterojunction INterlayer Tunnel Field Effect Transistor [1]. This name was coined by my student, Mingda Oscar Li, based on one of the device concepts we submitted in the LEAST center proposal. The rationale behind this device concept was derived from our earlier work on III-V based TFETs, in particular, TFETs with tunneling aligned with the gate field [2] and our investigations on the impact of band alignment (straddling [3], staggered and broken-gap [4]) on TFET. In the recent benchmarking exercise [5,6], a few more intriguing features were discovered in this 2D embodiment of the TFET with tunneling aligned with the gate field, in additional to being the ultimate scaled TFET down to the atomic thickness. [1] M. Li et al, JAP, 074508 (2014). [2] Y. Lu et al. EDL, 655 (2012). [3] G. Zhou et al. EDL, 782 (2012); G. Zhou et al. EDL, 1516 (2011). [4] G. Zhou et al. DRC (2011); G. Zhou et al. IEDM (2012). [5] M. Li et al. J-EDS, 200 (2015); [6] D. Nikonov et al., J. Exploratory Solid-State Computational Devices and Circuits, 10.1109/JXCDC.2015.2418033 (2015).

8:40am **EM-TuM3 Application of Thermodynamics to Processing Transition Metal Dichalcogenides**, ***Suzanne Mohney****, A.C. Domask, T.N. Walter, R.L. Gurunathan, Y. Zeng*, Penn State University

We have applied thermodynamics to guide us in processing transition metal dichalcogenides for ohmic contact formation, oxidation, and etching. Annealing has been reported by a number of researchers to reduce the resistance of electrical contacts to transition metal dichalcogenides. To better understand the effect of annealing and guide our ongoing experiments, we have surveyed the condensed phase equilibria in the transition metal-Mo-S systems. The phase diagrams we have calculated or found in the literature fall into three categories: the metal is in thermodynamic equilibrium with MoS2, there is a driving force for the metal to reduce MoS2, or there is a stable solid solution or ternary phase that dominates the phase diagram. We have performed a similar analysis of the metal-W-Se systems, although there is less thermodynamic data available for the transition metal selenides than the transition metal sulfides. In this presentation, we will first compare materials characterization of annealed contacts to MoS$_2$ and WSe$_2$ to our predictions. Then, we will turn our attention to oxidation and etching. Introducing transition metal dichalcogenides to an oxidizing environment can have different effects on the material, depending on the temperature and partial pressure of the oxidizing agent. Using O$_2$, we find from our thermodynamic calculations that a solid product of oxidation forms on MoS$_2$ and WSe$_2$ at mildly elevated temperatures, whereas at higher temperatures we can use O$_2$ as a vapor phase etchant due to the volatility of the oxygen-bearing reaction products. We have found good agreement between our predictions and characterization of processed samples using light microscopy, atomic force microscopy, scanning electron microscopy, and scanning Auger microscopy.

9:00am **EM-TuM4 Stress-Directed Compositional Patterning of SiGe Substrates for Lateral Quantum Barrier Manipulation**, *S. Ghosh,* University of New Mexico, *D. Kaiser,* University of Pennsylvania, *J. Bonilla,* University of New Mexico, *T. Sinno,* University of Pennsylvania, ***Sang M. Han***, University of New Mexico

For large-scale manufacturing of single-electron transistors, the capability to form an addressable 2D array of quantum dots would prove useful. While vertical stacking of quantum well and dot structures is well established in heteroepitaxial semiconductor materials, however, manipulation of quantum barriers in the lateral direction in a uniform array poses a significant engineering challenge. Here, we demonstrate lateral quantum barrier manipulation in a crystalline SiGe alloy, using structured mechanical fields to drive compositional redistribution. To apply stress, we make use of a nano-indenter array that is pressed against a Si$_{0.8}$Ge$_{0.2}$ wafer in a custom-made mechanical press. The entire assembly is then annealed at high temperatures, during which the larger Ge atoms are selectively driven away from areas of compressive stress. Compositional analysis of the SiGe substrates reveals that this approach leads to a transfer of the indenter array pattern to the near-surface elemental composition, resulting in near 100% Si regions underneath each indenter and a natural pathway to quantum barrier modulation. The process is studied in detail using multiscale computer simulations that demonstrate its robustness across a wide range of applied stresses and annealing temperatures. We computationally explore a carefully chosen set of indenter arrangements to show that Ge atoms can be focused into dots. We expect that this “stress transfer” method can be applied to other crystalline alloys in a scalable way.

9:20am **EM-TuM5 Interlayer Tunnel FETs**, ***Sanjay Banerjee***, Microelectronics Research Center, University of Texas at Austin **INVITED**

The scaling limits of conventional silicon based Complementary Metal Oxide Semiconductor (CMOS) devices has triggered a wide range of research in search of potential candidates for beyond CMOS logic devices. We will discuss the operation of vertical interlayer tunnel field effect transistors (ITFETs) using a stacked double bilayer graphene (BLG) and hexagonal boron nitride (hBN) heterostructure as one such potential candidate. The device is fabricated with a sequential pickup transfer method with the edges of the top and bottom BLG flakes being rotationally aligned to roughly 60° for alignment of the K points in the Brillouin zone of the two graphene layers, and using the hBN as the top, interlayer and substrate dielectric. The device shows multiple negative differential resistance (NDR) peaks which can be adjusted through the gate bias. Temperature dependent measurements show that the peak width of the differential conductance slightly broadens and the height somewhat lowered when the temperature is increased, but overall the temperature dependence is weak enough to be indicative of resonant tunneling being the primary mechanism. Through electrostatic calculations, it is shown that the multiple peaks occur when the two conduction bands at the K-point of the top and bottom bilayer graphene become aligned at certain bias conditions. It is also shown that by adjusting the rotational alignment of the bands of the top and bottom BLG through an in-plane magnetic field, the conductance peaks can be broadened or sharpened. As an example of a potential application, by utilizing the NDR characteristic of the device, a one-transistor latch or SRAM operation is demonstrated which operation margin can be adjusted through the gate bias.

11:00am **EM-TuM10 Graphene and TMD for Electronic Devices**, ***Seongjun Park***, *J. Lee, J. Heo, K. Lee, E. Lee, S. Lee, S. Jung*, Samsung Advanced Institute of Technology, Republic of Korea **INVITED**

Two dimensional (2D) materials including Graphene and Transition Metal Dichalcogenide (TMD) have been considered as potential materials for post Si technology. They are atomically thin and have exceptional electronic and optoelectronic properties, such as high electron mobility and high reponsivity. In addition, they have unique mechanical properties as inorganic semiconductors, such as flexibility and even some stretchabilities due to their atomic thin nature.

TMS's have band gaps and TMD based device can have high on/off ratio. Thus, they have been considered as channel materials for atomically thin nano devices. There are various TMD materials with various band gaps and this is somewhat advantages for TMD's since they can be considered many different applications depending on their band gaps.

Unlike TMD, graphene has no band gap and it is difficult to achieve high on/off ratio. We propsed and demonstrated a new device structure, Barristor, based on one of the unique properties of graphene, work function tunability. The key feature of the device is the modulation of Schottky barrier height between graphene and semiconductor through the gate voltage modulation. This new device shows high on/off ratio of 1,000,000 or higher can be achieved. In addition, Barristor is fully compatible with curent Si technology and we were able to fabricate the devices with 6" wafer scale with CVD (Chemical Vapor Deposition) grown graphene.

In this presentation, we will cover some of our recent developments of TMD based devices. We investigated various TMD's and we will present the summary of their performances. Also we will discuss about the details od Barristor including vertical tunneling devices. In addition, we will dIscuss the issues on wafer scale developments and some of the process related issues of TMD devices and Graphene Barristor and their potential applications.

11:40am **EM-TuM12 On Smart Textiles and Vacuum: The Joys of Innovation and Discovery on Quality of Life**, ***Sundaresan Jayaraman***, Georgia Institute of Technology **INVITED**

The discovery of vacuum has had a transformational impact on the quality of life of individuals. Until recently, the term "wearable" referred to a garment that is worn by individuals. However, the invention of the wearable motherboard or smart textiles has given new meaning to the term "wearables" and it goes beyond the traditional definition of clothing. Rather, it refers to an accessory that enables *personalized mobile information processing*.

We present the the concept of the wearable motherboard integrating electronics and textiles. We discuss the role of textiles as a "meta-wearable," and how it has transformed a multitude of disciplines ranging from sports to healthcare. Finally, we the discuss the future of smart textiles as a key enabler in the context of "big data," and its impact on the quality of life of individuals.

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

Photocatalysis
Moderator: Jason Baxter, Drexel University, Manjula Nandasiri, Pacific Northwest National Laboratory

8:00am **EN+AS+EM+SE+SS-TuM1 Ultra-dense Hydrogen and Low Energy Nuclear Reactions**, ***Sveinn Olafsson***, Science Institute, Physics department University of Iceland*, L. Holmlid*, University of Gothenburg, Sweden

For over the last 25 years the science of cold fusion/LENR has been researched around the world with slow pace of progress. Modest quantity of excess heat and signatures of nuclear transmutation and helium production have been confirmed in experiments and theoretical work has resulted in a flora of possible theoretical scenarios. [1-2]

Here we present energy production in several stages of surface processes that result first in the formation of Rydberg matter of Hydrogen [3] that can later condense in a new ultra-dense Hydrogen phase with 2.3 pm short bond distances. This phase is nuclear active showing break-even fusion reaction [7] under 100mW laser pulsing and slow spontaneous fusion occurring without laser pulsing[4,5,6]. The experimental work in around 30 publications is briefly reviewed and latest experimental results presented and discussed.

In that work high-energy particles are detected from the spontaneous processes using scintillation and other similar detectors. Both spontaneous line-spectra and a spontaneous broad energy distribution similar to a beta-decay distribution are observed indicating detection of particles such as muons. The broad distribution is concluded to be due to nuclear particles, giving straight-line Kurie-like plots. They are observed even at a distance of 3 m in air and have a total rate of 10^7-10^{10} s^{-1}. In the talk the link of these observation to Low energy nuclear reactions (LENR) or so called cold fusion will be discussed experimentally and theoretically.

1. The science of low energy nuclear reaction.

Storms E. World Scientific Publishing Company; **2007**.

2. The explanation of low energy nuclear reaction.

Storms E. Ienergy Press; **2014**.

3. Review paper: Experimental Studies and Observations of Clusters of Rydberg Matter and Its Extreme Forms Leif Holmlid. J Clust Sci (**2012**) 23:5–34

4. Spontaneous ejection of high-energy particles from ultra-dense deuterium D(0)

Leif Holmlid and Sveinn Ólafsson

Volume 40, Issue 33, 7 September **2015**, Pages 10559–10567)

5. Charged particle energy spectra from laser-induced processes: nuclear fusion in ultra-dense deuterium D(0) Leif Holmlid and Sveinn Ólafsson submitted **2015**.

6. Muon detection studied by pulse-height energy analysis: Novel converter arrangements

Leif Holmlid and Sveinn Ólafsson. Rev. Sci. Instrum. 86, 083306 (**2015**);

7. Heat generation above break-even from laser-induced fusion in ultra-dense deuterium

Leif Holmlid. AIP Advances 5, 087129 (**2015**);

8:20am **EN+AS+EM+SE+SS-TuM2 Optical and Surface Properties of Semiconductor Nanowires for Solar Fuels**, ***Eleonora Frau***, *J. Vukajlovic, A. Dalmau-Mallorqui, A. Fonctuberta i Morral, E. Alarcon Llado*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland

Semiconductor nanowires (NWs) are filamentary crystals with new properties from their bulk counterparts. Their large versatility makes them excellent candidates as building blocks for contributing to solving the energy problem in the near future. In this work, we will assess two main properties of semiconductor NWs that have an impact to solar energy conversion.

First, it is known that light is strongly absorbed by NW arrays since light resonances give rise to effective absorption cross-sections that are much larger than the geometrical ones. Optical resonances depend on NW geometry and dielectric environment, and can result into absorption effective diameters up to 25 times larger than the geometrical for certain wavelengths. We have used finite-difference time-domain (FDTD) electromagnetic simulations to understand and design NW-based sunlight scavengers. For instance, a GaAs NW array that is only covering 3% of the surface can generate more photocurrent than a planar film, considering a 30% reflectivity (see figure1). Also that thanks to optical resonances, an indirect-bandgap material such as Si is capable of absorbing most of the light within a 2um long NW array that only covers 7% of the device surface.

On the other hand, it is also known that surface states and traps detriment device performances. However, in case where solar energy is directly converted into fuel (such as hydrogen) in a photoelectrochemical (PEC) cell, the large surface-to-volume ratio of NW forests is an important asset. Since the electrochemical reactions happen at the semiconductor surface, NWs enable the use of low-cost catalysts (e.g. MoSx) even though they exhibit lower performances than noble metals (e.g. Pt). In order to assess the effects of nanostructuring photo-electrodes for solar fuel generation, we have studied photo-cathodes based on Silicon nanopillar structures. The photo-cathodes were fabricated by using a top-down approach and their diameters range from ~200 to 900nm and lengths ~2um. We observe that reducing the size of the nanostructure, increases the overpotential, and thus the overall efficiency (see figure 2). By coating the surface with thin TiO_2 layers, the performance is improved in terms of overpotential and fill factor. We explain these findings by using an electrico-kinetic model of the semiconductor-water junction. We find that the TiO_2 layers actually act as a hole blocking layer, preventing recombination.

8:40am **EN+AS+EM+SE+SS-TuM3 Engineering Surfaces and Interfaces for Photoelectochemical (PEC) Water-Splitting**, ***Thomas Jaramillo***, *J.D. Benck,* Stanford University*, J. Kibsgaard,* SLAC National Accelerator Laboratory*, T.R. Hellstern, C.J. Hahn, P. Chakthranont, R. Britto, K.D. Fong*, Stanford University **INVITED**

The talk will focus on engineering surfaces and interfaces for solar photoelectrochemical (PEC) water-splitting for the direct, renewable production of H_2. In particular, this talk begin by describing research efforts to develop H_2 evolution catalysts that are active, stable, and comprised of only earth-abundant elements, including transition metal sulphides, phosphides, and phosphosulfides.[1-3] Next, we will describe recent efforts to integrate these catalysts onto semiconductor surfaces to provide corrosion protection as well as enhanced interfacial catalysis for PEC water-splitting.[4] This talk will focus on the need for high turnover frequency (TOF) catalysts, which ultimately enable the greatest flexibility in designing optimum interfaces for high performance devices.

[1] J. Kibsgaard, T.F. Jaramillo, F. Besenbacher, "Building an appropriate active site motif into a hydrogen evolution catalyst with thiomolybdate $[Mo_3S_{13}]^{2-}$ clusters," *Nature Chemistry*, **6** (2014) 248.

[2] J.D. Benck, T.R. Hellstern, J. Kibsgaard, P. Chakthranont, T.F. Jaramillo, "Catalyzing the Hydrogen Evolution Reaction (HER) with Molybdenum Sulfide Nanomaterials," *ACS Catalysis*, **4** (2014) 3957.

[3] J. Kibsgaard and T.F. Jaramillo, "Molybdenum Phosphosulfide: An Active, Acid-Stable Earth-Abundant Catalyst for the Hydrogen Evolution Reaction," *Angewandte Chemie*, **53** (2014) 14433.

[4] J.D. Benck, S.C. Lee, K.D. Fong, J. Kibsgaard, R. Sinclair, T.F. Jaramillo, "Designing active and stable silicon photocathodes for solar hydrogen production using molybdenum sulfide nanomaterials," *Advanced Energy Materials*, **4** (2014) 1400739.

9:20am **EN+AS+EM+SE+SS-TuM5 Bulk and Surface Effects of Incorporating Titanium Into Hematite Thin Films to Improve Photoelectrochemical Water Splitting**, ***Anthony Abel***, *A.M. Patel,* Drexel University*, I.G. Torregrosa,* Utrecht University, Netherlands*, B. Opasanont, J.B. Baxter*, Drexel University

Hematite (α-Fe_2O_3) has emerged as a promising photoanode material for photoelectrochemical (PEC) water splitting due to its chemical stability, earth-abundance, low cost, and suitable band gap for both water splitting and visible light absorption. However, poor charge separation due to low hole mobility and high recombination rate, and sluggish oxygen evolution reaction kinetics have limited its potential as an economical water-splitting catalyst. Here, we investigate titanium incorporation into hematite photoanodes and provide insight into the role of Ti^{4+} in improving PEC performance. Planar hematite thin films (~45 nm thick) were deposited by successive ionic layer adsorption and reaction (SILAR) of FeOOH on an FTO/glass substrate and subsequent annealing to induce phase transition to α-Fe_2O_3, and titanium was incorporated up to 10% Ti/(Ti+Fe) by either modification of the SILAR solution (SM:α-Fe_2O_3) or solid-state diffusion (SSD:α-Fe_2O_3) during the annealing process. PEC measurements revealed substantial improvements in both charge separation efficiency and hole injection into the electrolyte, increasing photocurrent from nearly zero to ~0.6 $mAcm^{-2}$ under 1-sun irradiation at 1.23 V_{RHE}. Mott-Schottky analysis indicated a 100 mV cathodic shift in the flat band potential upon doping with Ti^{4+} regardless of fabrication method, but a 100-fold increase in carrier density only in SM:α-Fe_2O_3 films, resulting in a high 20 % separation efficiency at 1.23 V_{RHE} with optimized 5 % Ti/(Ti+Fe) in the modified SILAR solution. Electrochemical impedance spectroscopy showed a 4x increase in the surface state capacitance peak near the water oxidation onset potential, possibly due to reduced Fermi level pinning as a result of more efficient hole injection into the electrolyte . More importantly, doping with titanium resulted in a 100-fold decrease in the charge transfer resistance from surface states to the electrolyte, revealing the strong influence of Ti^{4+} on interfacial kinetics . Further surface modification with an ultrathin FeOOH surface passivation layer raised the plateau photocurrent to ~0.8 $mAcm^{-2}$ at 1.23 V_{RHE}, representing a 3x improvement over previous reports of SILAR-deposited hematite films and comparable with record performance for planar hematite deposited using high vacuum synthesis techniques.

9:40am **EN+AS+EM+SE+SS-TuM6 Iron Oxide Nanoparticle Growth on Highly Oriented Pyrolytic Graphite (HOPG) and Photocatalytic Properties of Pt on Iron Oxide**, ***Jayde Kwon***, *J.C. Hemminger*, University of California, Irvine

Highly oriented pyrolytic graphite (HOPG) is an ideal substrate to study the fundamental growth mechanism of iron oxide independent from substrate effects. Platinum on iron oxide is a model heterogeneous catalyst with importance to biotechnology and solar cell applications. Selective growth of iron oxide nanoparticle (NP) either on step edges of HOPG or oxygen plasma treated HOPG by physical vapor deposition (PVD) will be presented. The successful selective iron oxide NP growth was validated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The development of the NP array system is highly significant in that it can provide an ideal template for theoretical calculations for fundamental metal growth studies. Pt nanoparticles was subsequently deposited on the iron oxide nanoparticles using a selective photodeposition technique. The application of these nano-systems (Pt nanoparticles on iron oxide nanoparticles) towards photocatalysis of methylene blue will be presented. Although iron oxide is a promising semiconductor photocatalyst, it suffers from a short hole diffusion length, low electrical conductivity and a high rate of electron hole recombination. However, this bimetallic system using platinum deposited on iron oxide overcomes these barriers. A novel method was developed using small quantities of Pt on iron oxide to significantly enhance methylene blue decomposition. This system is also being explored as a catalytic model for water-gas shift reactions.

11:00am **EN+AS+EM+SE+SS-TuM10 Interface Design for Efficient and Stable Photoelectrochemical Water Splitting**, ***Joel Ager***, Lawrence Berkeley National Laboratory **INVITED**

Solar photoelectrochemical (PEC) water splitting is potential future carbon-neutral energy source which could dramatically change the landscape of global energy generation and storage. The half reactions for water splitting are as follows:

$2H^+ + 2\ e^- <-> H_2$ (1)

$H_2O <-> 2e^- +2H^+ + 1/2O_2$. (2)

The free energy change for the overall reaction, $H_2O <-> H_2 + 1/2O_2$ corresponds to 1.23 eV per electron transferred; however, typically >1.5 V is required to overcome kinetic limitations, particularly for the O_2 evolution reaction. The most commonly used approach for integrated solar water splitting employs photocathodes (H_2 or hydrocarbon producing) and photoanodes (O_2 producing) linked in a tandem geometry [1].

The interface challenges required to demonstrate a practical system which is both efficient and stable under operation are substantial and severe. In addition to constructing interfaces, either solid-solid or solid liquid, which achieve the desired photovoltaic charge separation, the surfaces of these photoelectrodes can be a failure point under sustained operation due to corrosion. We have found that the use of nanoscale conformal oxide layers can greatly reduce corrosion rates. Moreover, it is possible to achieve both high performance and lifetime by the use of protection layers which are also tuned for selective carrier contact.

Examples of such a strategy will be shown for photocathodes [2-5] and for photoanodes [5]. Recent work on p-type transparent oxides (p-TCOs) used as selective hole contacts for photoanodes will be emphasized. For example, it will be shown that using $NiCo_2O_4$ as the p-TCO and n-type Si as a prototypical light absorber, a rectifying heterojunction capable of light driven water oxidation can be created. By placing the charge separating junction in the Si using a np^+ structure and by incorporating a highly active Ni-Fe oxygen evolution catalyst, efficient light-driven water oxidation can be achieved. The generality of the p-TCO protection approach is demonstrated by multi-hour, stable, water oxidation with n-InP/p-$NiCo_2O_4$ heterojunction photoanodes.

Acknowledgements. This material is based upon work performed by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, supported through the Office of Science of the U.S. Department of Energy under Award Number DE-SC0004993.

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2. M. H. Lee *et al*., *Ang. Chemie Int. Edition***51** 10760 (2012).

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11:40am **EN+AS+EM+SE+SS-TuM12 Buried, Hetero, and p-i-electrolyte III-V Photoelectrochemical Junctions with Significantly Enhanced Photocurrent Onset Potentials**, ***James Young****, H. Doscher, J. Turner, T. Deutsch*, National Renewable Energy Laboratory

To approach the maximum achievable solar-to-hydrogen (STH) conversion efficiencies with photoelectrochemical (PEC) devices, it is necessary to employ the lowest possible band gap (E_g) absorbers that can still provide sufficient voltage to drive water splitting at high rates (1.7-1.8 V for 25% STH). The record 12.4% STH was achieved by a $GaInP_2$/GaAs PEC/photovoltaic (PV) tandem device while an all solid state $GaInP_2$/GaAs PV/PV tandem produces an open-circuit voltage that approaches 2.4 V. Since GaAs (E_g = 1.4 eV) is the current-limiting junction in these devices, it can be substituted by InGaAs with E_g = 1.0 eV to reach 25% STH. The current-for-voltage tradeoff of using lower-E_g absorbers moves toward the constraint of insufficient voltage for spontaneous water splitting. To address this approaching constraint, we investigate several alternative device structures at the III-V/electrolyte interface that show photocurrent onset potential enhancements of a few hundred mV. We will present band diagram calculations and electrochemical measurements to discuss the voltage performance of these structures.

12:00pm **EN+AS+EM+SE+SS-TuM13 X-ray Absorption Studies on the Li-S Battery Cathode Side**, ***Yifan Ye,*** University of Science and Technology of China*, A. Kawase,* Lawrence Berkeley National Laboratory*, H.X. Ju,* University of Science and Technology of China*, E. Cairns,* Lawrence Berkeley National Laboratory*, J.-H. Guo,* Lawrence Berkeley Lab, University of California, Berkeley*, J.F. Zhu*, University of Science and Technology of China

As increasing global energy consumption in the coming days, sustainable, clean energy technologies are highly desirable. The high theoretical specific capacity of 1675 mA·h/g for elemental S has prompted intense effort to study the Lithium-Sulfur batteries. With the application of cetyltrimethyl ammonium bromide (CTAB), modified sulfur-graphene oxide (S-GO) nano-composite based Li/S batteries exhibited a very high initial discharge capacity of 1440 mA·h/g of sulfur at 0.2C with excellent rate capability of up to 6C for discharge and 3C for charge while still maintaining high specific capacity. And the batteries demonstrated cycling performance up to 1500 cycles with extremely low decay rate of 0.039% per cycle. With the introduction of CTAB, the performance of the GO-S based Li-S battery has been improved significantly, thus it is important to figure out the role of CTAB played in the system. During the synthesis process of the cathode materials, S and Na_2S were used as the precursors, the ratio of S/Na_2S is crucial to the components of the precursors. Moreover, the sequence of mixing GO/CTAB solution with precursor solution is a key point to effective cathode synthesis procedure. Understanding these information helps to optimize the methodology for the controllable synthesis of desired cathode material that can be used to fabricate an efficiency and well-performed Li/S battery. S K-edge X-ray absorption spectroscopy (XAS) is applied to study the chemical species evolution during the GO-S-CTAB cathode material synthesis. The influences on the cathode materials related to the battery performance are monitored by S K-edge XAS. The research revealed the interaction between CTAB and GO, S, Na_2S and Na_2S_x. It indicated that CTAB can physical absorbed on Na_2S_x molecules by bonding with the terminal S atoms of Na_2S_x chains, and this kind of bonding can convert to chemical C-S bonding with heating treatment. Thus the interaction of CTAB with GO, formed C-S between CTAB and S and interaction of GO and S provided a tight tri-layer structure which can immobilize the S particles on GO sheet and finally enhanced the battery performance. The information from this work proved the importance of Na_2S:S ratio, CTAB/GO adding procedure in the fabrication process, and we can easily apply XAS to optimize these recipe. And moreover, this work proved strong evidence that XAS tools can be used to do the initial characterization on the battery performance before real cycling procedure.

Exhibitor Technology Spotlight
Room: Hall 1 - Session EW-TuM

Exhibitor Technology Spotlight Session
Moderator: Dennis Sollon, Kurt J. Lesker

10:20am **EW-TuM8 Ask the Experts Special EW Session***, **Gerardo Alejandro Brucker***, MKS Granville-Phillips Division, Longmont

The presentation will include a primer on the principles of vacuum technology including: vacuum generation, gas flow and pressure measurement along with discussion of the most interesting questions and challenges raised by the AVS audience throughout the years. Learn the differences between direct and indirect pressure measurement. Understand the advantages of thermal versus pressure based mass flow controllers. If you are new to the vacuum industry or are interested in hearing what your colleagues are doing with vacuum technology this is a great opportunity to learn some new and interesting tricks." After the spotlight presentation, be sure to visit the Ask-the-Experts booth (#439) where you will find a wide group of international experts who volunteer their time to answer vacuum process and technology questions from the conference attendees. Over the many years that the event has been hosted by the AVS, there have been many interesting questions asked by the AVS community and answered by a wide range of experts. The goal of this presentation is to bring awareness to this sponsored event and to discuss some of the most interesting questions fielded by the general AVS audience during the last few conferences.

10:40am **EW-TuM9 The Nano Probe Station for Your 2D Characterization Needs: The First Low Temperature MultiProbe SPM-NSOM System Integrated with Raman***, **Aaron Lewis***, Nanonics

The Nanonics CryoView MP is the ideal SPM platform for studying mechanical, optical, electrical, thermal and chemical nanoscale properties of 2D materials at low temperature. Materials such as graphene, hexagonal boron nitride (h-BN), dichalcogenides (e.g.) MoS2, etc. The CryoView MP is uniquely suited to conduct studies in dynamics, photoconductivity, electrical conductivity, and other phenomenon of such materials. Very sensitive and stable tip-sample interaction control through the tuning fork feedback mechanism allows for high resolution SPM measurements. The open optical access allows for a variety of optical integrations including near-field, Raman, TERS and fluorescence measurements. Multiple online probes allow for a variety of measurements including MFM, EFM, SSRM, KPM, SThM, and NSOM. The CryoView MP opens up many new possibilities for exciting research in your 2D materials.

IPF on Mesoscale Science and Technology of Materials and Metamaterials
Room: 210F - Session IPF+MS-TuM

Degradation Science (8:00-10:00) & Electrochemistry from Nano to Meso Scale (11:00-12:20)
Moderator: Gary Rubloff, University of Maryland, College Park, Stacey Bent, Stanford University

8:00am **IPF+MS-TuM1 Mesoscale Evolution & Temporal Analytics of Photovoltaic Energy Materials: A Degradation Science Approach**, ***Roger French***, Case Western Reserve University **INVITED**

Degradation science1 combines physical and statistical approaches to examine degradation mechanisms and pathways of a material or system in order to improve materials and reduce system failures by incorporating modeling, monitoring, and prediction of lifetime performance. Degradation of PV modules evolves over long time-frames and length scales, which is a characteristic of mesoscale science. Degradation arises due to the distinct, complex, and interactive phenomena which lead to failure. Real-world studies under diverse environmental conditions must be combined and cross-correlated with accelerated in-lab studies, using data science and analytics methodologies, so as to span the time and length scales that control the system's behavior over lifetime. Semi-supervised generalized structural equation (semi-gSEM) modeling can be used to relate physical mechanistic submodels with data-driven statistical submodels as networks of mechanisms and modes with statistically significant pathway relationships. The relationships and coupling strengths (βij) amongst variables can be rank-ordered in their contributions to the system's degradation. Temporal evolution, damage accumulation and change points among mechanisms/modes (variables) are accounted for in the semi-gSEM models. Towards these goals, a statistical methodology has been developed and applied to investigate the response of full sized PV modules to accelerated stress conditions. The results of this initial study indicate that a correlation exists between system level power loss and the buildup of acetic acid resulting from the hydrolytic degradation of EVA polymer encapsulant. To further explore this proposed mechanistic pathway, studies are underway to characterize the degradation of minimodule samples under a broader range of similar multifactor accelerated stress conditions. Sample types feature frontside silver gridlines of two different widths and exposure conditions vary in irradiance level and temperature. Samples are measured non-destructively at many points along their lifespan, using confocal Raman microscopy to capture chemical signals and various techniques to gather electrical performance information, with the goal of observing the co-evolution of EVA degradation and gridline corrosion. This represents an important first step towards exploring the often misunderstood role of EVA degradation in PV module performance loss, and building a more integrated picture of PV module degradation as a whole. Initial data analytics of six months' real-world performance data of 60 c-Si PV modules on the SDLE SunFarm shows deviation of performance ratio among modules at the same geometric location. Grouping of samples with similar performance patterns was performed with hierarchical clustering, K-means clustering was used to confirm the optimum number of clusters. A brand dependent module performance model was developed based on a subgroup of 21 modules from 7 manufactures. Over 1.5 million I-V curves measured every 5 minutes for 500 days on 10 modules with/without mirror on dual-axis trackers were analyzed use an automated analytic functions we developed. Maximum power point, open circuit voltage, short circuit current, slope of the curve near open circuit voltage, and slope of the curve near short circuit current are either directly extracted or estimated from measured I-V curves. An algorithm based on moving local regression model was developed to detect the change points on I-V curves, which caused by bypass diode turning on when I-V curve was measured under non-uniform irradiance. These examples of the use of degradation science, with its physical and statistical foundation and data analytics approach, will hopefully enable the community to address the long-term reliability uncertainty of photovoltaics as they become a major component in the world's energy systems.

1. French, Roger H., Rudolf Podgornik, Timothy J. Peshek, Laura S. Bruckman, Yifan Xu, Nicholas R. Wheeler, Abdulkerim Gok, et al., 2015, "Degradation Science: Mesoscopic Evolution and Temporal Analytics of Photovoltaic Energy Materials," Current Opinion in Solid State and Materials Science, Doi: 10.1016/j.cossms.2014.12.008

8:40am **IPF+MS-TuM3 Why Structural Failure is Mesoscale: From Dislocations to Fatigue Cracks**, ***Anthony Rollett***, Carnegie Mellon University **INVITED**

Structural failure of materials is a mesoscale problem because, for example, we lack the tools to predict when and where fatigue cracks will appear in relation to materials microstructure. Dislocations are well understood as line defects but we do not how to compute the behavior of large numbers of dislocations in relation to microstructure. Enormous strides have been made in quantifying the growth of fatigue cracks over the years and improving predictions of component lifetime but all at the microstructural scale and above. Nevertheless, it is clear that the behavior of short cracks is less well quantified, where short is relative to the length scale(s) found in materials microstructure, e.g. grain size. Short fatigue cracks in nickel-based superalloys have been characterized using conventional SEM and orientation mapping. High Energy Diffraction Microscopy (HEDM) and computed tomography (CT) was used to map out the crack positions in 3D. The main finding is that cracks develop most readily along long twin boundaries with high resolved shear stress on the slip systems parallel to the twin plane. Also, both halves of a different superalloy, fully fractured sample have been fully characterized in 3D using the same tools. The HEDM and CT were performed with high energy x-rays on beamline 1ID at the Advanced Photon Source (APS). This talk will review current dislocation modeling, empirical understanding of fatigue cracks in engineering materials and what the experimental and theoretical roadmap might be to address the problem set.

9:20am **IPF+MS-TuM5 Engineered 3D Mesoscale Battery Electrodes: Opportunities and Issues**, ***Paul Braun***, University of Illinois at Urbana-Champaign **INVITED**

Over the past decade, three-dimensional structures have been widely proposed as a path for enhanced lithium-ion batteries. While the sophistication of self and directed-assembly approaches for functional structures has increased dramatically, application of these structures has remained elusive, in part because real structures almost always contain finite defect densities, cannot be produced from materials with the appropriate electrochemical properties, and cannot be produced in sufficient volume for application. We have now made considerable strides in integration of electrically conducting and energy storage material into lithium-ion battery electrodes. We accomplish this by applying template-based and post-synthetic materials transformations, and have focused on ultra-large volume processing strategies. As the technology has approached commercialization, understanding the mechanistics of capacity fade and other electrochemical degradation pathways has become increasingly important.

11:00am **IPF+MS-TuM10 A Materials Genome Approach to Design of Novel Materials and Liquids for Energy Conversion and Storage**, ***Kristin A. Persson***, Lawrence Berkeley National Laboratory **INVITED**

The Materials Genome Initiative (MGI) aims to develop an infrastructure to discover, develop, manufacture, and deploy advanced materials at least twice as fast as possible today, at a fraction of the cost. In this talk I will highlight the advances and development of the Materials Project (www.materialsproject.org), which is an MGI-funded effort to compute the properties of all known inorganic materials and beyond, design novel materials and offer data to the community together with online analysis and design algorithms.1 The current release contains data derived from density functional theory (DFT) calculations for over 60,000 materials, each with searchable associated properties such as relaxed structure, electronic state, energy storage capability, aqueous and solid stability, and more. The software infrastructure enables thousands of calculations per week – enabling screening and predictions - for both novel solid as well as molecular species with target properties. Current application areas include photocatalysis, thermoelectrics, beyond-Li energy storage, and alloy design.

To exemplify the approach of first-principles high-throughput materials design, we will make a deep dive into future energy storage technologies, showcasing the rapid iteration between ideas, computations, and insight as enabled by the Materials Project infrastructure and computing resources. To understand and design novel electrodes for multivalent energy storage requires efficient and robust evaluation of stability, voltage, capacity, volume change, and most importantly, active ion mobility, which is the foremost bottleneck in these systems. Understanding of the structural and chemical features – extracted from calculations and benchmarked against available experimental data - which correlate with facile, selective ion diffusion will be presented and discussed. We are also devoting a large effort to understanding, screening and designing organic liquid electrolyte systems for novel energy storage systems for which the bulk solvation structure and its impact on electrolyte performance is largely uncharted. As an example, we find that contact ion-pair interaction is prevalent in multi-valent electrolytes, even at modest concentrations which influences charge transfer, conductivity and even the stability of the electrolyte.

11:40am **IPF+MS-TuM12 Electrical Double Layer Effects on Ion Transport in Thin-Layer Solid-State Electrolytes**, ***Henry White***, *J. Xiong*, *M. Edwards*, University of Utah **INVITED**

We present finite-element modeling of Li^+ transport in solid-state electrolytes, including the role of the double layer electric fields. We developed a 1-D model that describes the mass transport and electric potential, assuming that Li^+ is the predominant charge carrier. Mass transport is described by the Nernst-Planck equation and the electric potential is described by Poisson's equation. These equations were solved in a fully coupled manner, i.e., the electric field affects the mass transport through the electromigration term in the Nernst-Planck equation, while the excess charge due to unequal ion concentrations affects the electric field as the space charge term in Poisson's equation.

We present calculated potential and concentrations distributions, as well as the contributions of migration and diffusion to the flux of each species. We present investigations of the effect of the solid-state electrolyte thickness on mass transport, varying the thickness from 10 nm to 2000 nm. The current normalized to electrolyte thickness is shown to decreases as the thickness decreases.

In-Situ Spectroscopy and Microscopy Focus Topic
Room: 211C - Session IS+AS+SA+SS-TuM

In-situ Studies of Solid-liquid Interfaces
Moderator: Anatoly Frenkel, Yeshiva University, Franklin (Feng) Tao, University of Kansas

8:20am **IS+AS+SA+SS-TuM2 Water at Ionic Liquid Interfaces Probed by APXPS**, ***John Newberg***, *Y. Khalifa*, *A. Broderick*, University of Delaware

Ionic liquids (ILs) have a wide array of applications in biotechnology, coatings, synthesis, separations, and energy sciences. Many of these processes involve either IL-solid or IL-vapor interactions. It is therefore critical we understand the fundamental interfacial properties of ILs on a molecular level. Due to the ubiquity of water, its influence on the properties of ILs has been the focus of many bulk studies and, more recently, surface science studies. Here we will highlight the use of a recently commissioned ambient pressure X-ray photoelectron spectroscopy setup in our laboratory and its application in characterizing the interfacial region of hydrophilic and hydrophobic ILs upon interaction with water vapor as a function of increasing pressure.

8:40am **IS+AS+SA+SS-TuM3 Probig the Liquid-Solid Interface of polycrystalline Pt in 1.0 M KOH using Ambient Pressure Photoemission Spectroscopy and "Tender" X-rays**, ***Marco Favaro***, *B. Jeon, P.N. Ross, Z. Hussain, J. Yano, Z. Liu, E.J. Crumlin*, Lawrence Berkeley National Laboratory (LBNL)

With the previous success in soft X-ray AP-XPS gas-solid interface[1a-e] probing, researchers have started to gain insights into the liquid-solid boundaries[1d]. Taking the cue from these new research frontiers, we have developed on BL 9.3.1 at the Advanced Light Source (LBNL) a new liquid phase AP-XPS system (based on a Scienta R4000 HiPP-2 analyzer) that will shed new light on the understanding of the chemical changes at the electrode surfaces during normal working conditions, leading to a great enhancement of our knowledge on the most important processes in energy conversion and storage[2a,b]. The combination of this new system with synchrotron radiation in the “tender” X-ray region (between 2 and 7 keV), allows us to probe the interface between thin liquid and solid phases using high kinetic energy photons and then, thanks to the in operando approach, directly track the phenomena occurring at the electrode liquid-solid interface during the electrochemical reactions of interest. The technique developed at BL 9.3.1 allows the study of both gas-liquid and liquid-solid interfaces, for pressures up to a hundred of Torr[2a].

In order to deeply investigate the possibilities offered by this new technique and, at the same time, to establish a benchmark, a reference material such as polycrystalline Pt has been studied in 1.0 M KOH electrolyte. In this talk we will demonstrate that it is possible to have fine control of the applied potential[2a,b], measuring the core level binding energy shift of the of the oxygen *1s* and potassium *2p* photoemission lines, according to the applied external potential. Moreover we will discuss the observation, under *in operando* conditions, of the changes of the surface oxidation state[2b] of Pt triggered by the applied potential. Thanks to the innovative experimental approach, we have observed the *in situ* formation of Pt(II) and Pt(IV) species during the oxygen evolution reaction (OER), as well as the reversibility of the surface chemistry passing from anodic to cathodic potentials (up to the hydrogen evolution reaction, HER).

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[1] a. Lu et al., *Sci. Rep.* **2**, 715 (2012); b. Zhang et al., *Nat. Mat.* **9**, 944 (2010); c. Axnanda et al., *Nano Lett.* **13**, 6176 (2013); d. Starr et al., *Chem. Soc. Rev.* **42**, 5833 (2013); e. Mudiyanselage et al., *Angew. Chem. Int.Ed.* **52**, 5101 (2013).

[2] a. S. Axnanda, E. Crumlin et al., *Sci. Rep.*, accepted; b. E. Crumlin et al., *in preparation*.

9:00am **IS+AS+SA+SS-TuM4 Toward Ambient Pressure Electron Spectroscopy with Conventional XPS Instrumentation**, ***Andrei Kolmakov***, National Institute of Standards and Technology (NIST)

The current state of the art instrumentation for ambient pressure electron spectroscopy requires highly specialized sophisticated laboratory equipment or dedicated synchrotron radiation facilities. The limited access to these equipment impedes in situ (in vivo) studies under realistic conditions in catalysis, energy, environmental and bio-(medical) fields. We propose a new sample platform which enables ambient pressure XPS to be conducted using conventional XPS instrumentation. The core of the sample platform is microchannel environmental cells sealed with electron transparent, molecularly impermeable, mechanically and chemically stable graphene layer. The channels can be impregnated with liquids or gases and yet be vacuum compatible. Two major wafer scale fabrication strategies: (i) transferred graphene and (ii) as grown graphene layer were described. The coverage yield, membrane cleanness and leaking rates were comparatively studied. The feasibility tests of the platform included in situ XPS and electron microscopy studies of the water radiolysis and electrochemical processes taking place at liquid electrolyte-solid interface.

9:20am **IS+AS+SA+SS-TuM5 Solvation and Chemistry at the Interface: Near Ambient Pressure Electron Spectroscopy Studies of Aqueous Solution Interfaces**, ***John Hemminger***, University of California, Irvine **INVITED**

We have combined liquid-jet photoelectron spectroscopy coupled with classical molecular dynamics simulations to study the composition and chemistry of the liquid/vapor interface of aqueous solutions. Our experiments take advantage of the variable x-ray energy capability of synchrotron radiation and the kinetic energy dependence of the electron inelastic mean free path to carry out experiments with different probe depths. At low x-ray energy the low energy photoelectrons are detected primarily from the surface region of the solution. At higher x-ray energy our experiments probe more deeply into the solution. This allows us to directly compare the liquid/vapor interface with the bulk of the aqueous solution. We will present recent results on aqueous solutions of organonitrile compounds (acetonitrile and propionitrile). Our experiments and MD simulations show that both acetonitrile and propionitrile accumulate at the liquid/vapor interface—even though both nitriles are fully miscible with water. We have also studied the salting in and salting out effects for nitriles in water. We also have studied the effect of ion size on the surface propensity of cations in alkali halide aqueous solutions.

11:00am **IS+AS+SA+SS-TuM10 In situ Single-molecule Microscopy of Photoelectrocatalysis for Solar Water Oxidation**, ***Peng Chen***, Cornell University **INVITED**

This talk will present our recent results in using single-molecule super-resolution fluorescence microscopy to image photoelectrochemical reactions on single semiconductor nanostructures in situ under photoelectrochemical water oxidation conditions. We separately image hole and electron induced reactions, driven by light and electrochemical potential, and map the reactions at single reaction temporal resolution and nanometer spatial resolution. We also correlate the surface hole and electron reactivity with the local water oxidation efficiency using sub-particle level photocurrent measurements. By depositing oxygen evolution catalysts in a spatially controlled manner, we further identify the optimal sites for catalyst deposition for photocurrent enhancement and onset potential reduction.

11:40am **IS+AS+SA+SS-TuM12 *In Situ* and *Operando* AP-XPS for the Oxidation State of Pd at Solid/Liquid Interface**, ***Beomgyun Jeong***, *M. Favaro, P.N. Ross, Z. Hussain,* Lawrence Berkeley National Laboratory (LBNL)*, Z. Liu,* Shanghai Institute of Microsystem and Information Technology, China*, B.S. Mun, J. Lee,* Gwangju Institute of Science and Technology, Republic of Korea*, E.J. Crumlin*, Lawrence Berkeley National Laboratory (LBNL)

A catalyst is defined as a substance that enhances a reaction rate without changing its chemical state. However, often the chemical state of a catalyst surface undergoes changes during the reaction, leading to the degradation of catalyst performance. These phenomena are particularly significant in electrocatalysis in which reaction occurs at solid/liquid interface with electrical potential as an activation energy to drive the reaction. In order to understand the mechanism of catalyst degradation, it is important to have a capability to observe the chemical states of electrode and various chemical species in electrolyte during the reaction taking place at the solid/liquid interface. In order to explore this region, we have developed a new experimental approach [1], using ambient pressure XPS (AP-XPS) coupled with “tender” X-rays (in the range between 2.5 and 7.0 keV) at the Advanced Light Source BL 9.3.1, Lawrence Berkeley National Laboratory. Because of the relatively high kinetic energy of the incoming photons, ‘tender’ X-rays allow probing solid/liquid interfaces through thin electrolyte films characterized by a thickness of 10-30 nm. This unique functionality allows the ability to simultaneously correlate the electrocatalytic activity of electrodes to both the chemical modifications of the electrode surface, and the electrolyte.

This talk will provide details on *in-situ* and *operando* AP-XPS measurements on the chemical modifications of polycrystalline Pd surface studied at different electrochemical potentials. Pd is a cost-effective materials alternative to Pt showing similar electrocatalytic property of Pt in various reactions, such as oxygen reduction and electrooxidation of hydrogen and formic acid. On the other hand, it is well known that the Pd activity decreases faster than that of Pt especially in formic acid oxidation [2]. This phenomenology could be understood by the direct observation of the Pd surface chemistry evolution at electrified solid/liquid interface. We will discuss the performance of the Pd electrode in two different aqueous electrolytes, in particular in an alkaline medium and in a formic acid solution, an electroactive liquid organic molecule. We believe that our findings represent a step forward in the rationalization of the electrocatalytic behavior of Pd.

[1] S. Axnanda, E.J. Crumlin *et al.*, *Sci. Rep.* 5 (2015) 9788.; b. E.J. Crumlin *et al.*, in preparation.

[2] H. Jeon, S. Uhm, B. Jeong, J. Lee, *Phys. Chem. Chem. Phys.* 13 (2011) 6192.

12:00pm **IS+AS+SA+SS-TuM13 In situ Characterization of Switchable Ionic Liquids by Liquid ToF-SIMS and SALVi**, ***Juan Yao***, *X. Sui, D. Lao, Y. Zhou, S. Nune, D. Heldebrant, Z. Zhu, X.-Y. Yu*, Pacific Northwest National Laboratory

A vacuum compatible microfluidic reactor, SALVI (System for Analysis at the Liquid Vacuum Interface) was employed for *in situ* chemical imaging of switchable ionic liquids (SWILs) using time-of-flight secondary ion mass spectrometry (ToF-SIMS). A model SWIL system consisting of 1,8-diazabicycloundec-7-ene (DBU) and 1-hexanol with CO_2 gas to change solvent polarity was selected. A series of ionic liquids with different CO_2 loading was analyzed. Spatial chemical differences were observed within the same ionic liquid, indicating inhomogeneity of the ionic liquid. Spectral principal component analysis (PCA) was conducted using both positive and negative ToF-SIMS data. Clear distinctions were observed among SWILs of different CO_2 loadings. The loading plots strongly indicate that fully loaded SWILs share similar spectral components as those of the non-loaded Ils. This finding confirms the hypothesis of the biphasic structure in the fully loaded IL predicated by molecular dynamic simulation and presents the first physical evidence of the liquid microenvironment of IL determined by liquid ToF-SIMS. Various ion pairs were also observed in addition to the known SWIL chemistry of the DBU and 1-hexanol system, indicating the complexity of the ionic liquid previously unknown. The vacuum compatible microchannel in SALVI provides a new way to study ionic liquids in vacuum by sensitive surface techniques. Our approach directly visualized spatial and chemical heterogeneity within the SWILs by dynamic liquid ToF-SIMS for the first time.

Materials Characterization in the Semiconductor Industry Focus Topic
Room: 114 - Session MC-TuM

Characterization of 3D structures
Moderator: Paul van der Heide, GLOBALFOUNDRIES, Inc.

8:00am **MC-TuM1 Expanding Roles of Materials Characterization and Metrology in Advancing Moore's Law**, *Z. Ma*, ***Ying Zhou***, Intel Corporation **INVITED**

Moore's law scaling in the past decade was propelled by important technology breakthrough and innovation. Wide acceptance of popular low power devices such as smartphone and tablet continues to drive dimension scaling to achieve desired performance, power consumption and cost. However, traditional geometrical scaling for devices and interconnects encountered some fundamental material issues and scaling limits. To address these challenges, new classes of materials and device structures are being investigated for possible applications. The evaluation and introduction of disruptive process technologies and novel devices are driving strong interests in new material characterization techniques and methods. Process monitoring and control put stringent requirements on metrology capabilities at both technology development and manufacturing stages. This presentation will talk about the growing needs for materials characterization and metrology and their pivotal roles in enabling technology breakthrough and manufacturing sustaining. A comprehensive metrology approach is recommended to push ultimate analytical capabilities and accuracy while delivering required measurement consistency and data turns through automation and design for metrology.

8:40am **MC-TuM3 X-ray based Characterization of Strained SiGe on FinFETs**, ***Kriti Kohli***, *M.A. Smith, A. Madan, Z. Zhu, J.R. Holt*, GLOBALFOUNDRIES, *M. Klare*, Revera

The introduction of complex three-dimensional structures in device design presents challenges that require ever more sophisticated metrology with high accuracy and precision. One such example is the measurement of composition and thickness of epitaxially grown thin films on fins. Due to the preferential growth in the <111> plane of SiGe on fins, the film creates complex multi-faceted shapes on top of the fins. These 3D structures are challenging even for reference metrology to characterize due to the effects of shading and variability in geometrical area. The goal is to develop an inline metrology that measures composition and thickness of epitaxially grown SiGe directly on fins since blanket pads are no longer correlated to device performance. In this paper, we present a comprehensive characterization of a set of samples with varying geometry, thickness, strain and composition of SiGe films on fins using HRXRD, XPS, XRF and compare to reference metrology. With each technique, we have developed a methodology for measuring directly on 3D fins and compare the techniques to determine the most robust, precise and accurate metrology solution.

9:00am **MC-TuM4 Atomic Scale Analysis by Atom Probe on 3D Semiconductor Structures**, ***Ajay Kumar Kambham***, *S. Shintri, D. Flatoff, P. van der Heide*, Globalfoundries

Device structures are rapidly scaling down to the nanometer regime with the ongoing development in semiconductor device technology. Along with this, it is ever critical need to engineer dopant profiles and to define the formation of junctions in Metal-oxide field effect transistors (MOSFETs). This is increasingly challenging considering the severity of short channel effects (SCEs). Indeed, one type of SCE in MOSFET devices known to cause performance degradation is Drain Induced Barrier Lowering (DIBL). To reduce DIBL, dopant junction profiles are made more abrupt. This can be done through the introduction of Sigma/cavity structures and the modulation of stress through optimal engineered epitaxial buffer layers. To assess the quality over nanometer scale regions requires the use of analysis techniques such as Atom Probe Tomography (APT) and Transmission Electron Microscopy (TEM). This presentation will discuss the role of APT and how elemental distributions vary depending on type of faces employed, i.e. Si (100) vs Si (111) along with the challenges involved in sample preparation.

9:20am **MC-TuM5 Preparing and Characterizing Nanoscale Topological Insulators**, ***Kenneth Burch***, Boston College **INVITED**

Topological Insulators present new opportunities to control and manipulate spin in future nano-devices. A key difficulty has been realizing the rather high mobilities they promise and detecting unambiguous signatures of surface transport at high temperatures. I will discuss our groups efforts to prepare these materials on the nano-scale using mechanical exfoliation on various substrates with the aim of understanding the role of the substrate in their transport properties. In addition I will discuss the various optical probes (Raman and Infrared) we have applied to understand the phonons and their role in limiting the surface transport properties of these materials.

11:00am **MC-TuM10 "More than Moore": Could Silicene Be the Future of Electronics?**, *J. Avila, Ch. Chen, S. Lorcy*, ***Maria Asensio***, Synchrotron SOLEIL, France

For more than forty years, the miniaturization of circuits by scaling down the transistor has been the principal driver for the semiconductor technology. As the number of components per chip increases, the total chip size has to be reduced within workable limits. Consequently, the technology roadmap for semiconductors or "Moore's Law"(1), which states that the number of components integrated in a circuit would increase exponentially over time, has been successfully achieved by a continuous downscaling of the critical dimensions in the integrated circuit. Hence, since 1970, the number of components per chip has doubled every two years. However, we are nowadays nearing the basic limits of the scaling, thus for further improvement we may need "More than Moore"(2). This new attractive trend adds value to devices by incorporating more functionalities to them, which do not necessarily scale according to Moore's Law. Graphene is one of the best-placed novel materials to be included in a "More than Moore" approach. A close relative of graphene, a 2D honeycomb lattice of Si atoms called Silicene has been recently reported as nanoribbons and single layers on silver (111) oriented monocrystals, (3,4). As silicon, unlike carbon, prefers sp3 hybridization instead of sp2 hybridization, silicone possess several stable buckled structures, which are compatible with the opening of a small gap (5). This ability makes silicene very attractive to be integrated to the already well-developed silicon-based electronics.

The task to create a new "fabric" as silicene has been, however, very difficult because silicene does not exist in Nature and it is not as easy to form as graphene due surely to its particular electronic structure and larger atomic size. Over the last decade, research groups from around the world have claimed to have prepared silicene, a one atom-thick layer of silicon. However, just recently our team has created silicone single sheets of silicon on silver single crystal surfaces and has further characterized this novel material; using atomic resolution STM spectroscopy and high-resolution angle resolved photoemission, proving unambiguously the existence of one of the most stable phases of this unique material. (3)

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in Proc. IEEE, 86, 82 (1998).

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(3) P. Vogt, et al., Phys. Rev. Lett. 108, 155501 (2012)

(4) P. De Padova et al., Appl. Phys. Lett. 96, 261905 (2010)

(5) S.S. Cahangirov, et at., Phys. Rev. Lett. 102, 236804 (2009)

(6) S.S. Cahangirov, et at., Phys. Rev. B 90,(3) ,035448(2014)

11:20am **MC-TuM11 Challenges in Measuring Strain in Nanoscale 3D FinFET Structures**, ***Anita Madan***, GLOBALFOUNDRIES, *S. Mochozuki,* IBM Albany Nanotech Center, *C. Murray,* IBM, T. J. Watson Research Center, *D. Cooper,* CEA, LETI, MINATEC Campus, France, *Y. Wang, W. Weng, T. Pinto*, GLOBALFOUNDRIES

Strain engineering has been adopted as a key element for scaling high performance complementary metal-oxide-semiconductor (CMOS) devices. Complex 3D structures (FinFETs) have been introduced for the 14 nm technology node and beyond. Typically, strain is introduced by replacing the Si channel with SiGe for pFET devices. Characterization of strain in the fins is challenging due to the complexity of their three-dimensional geometries and their nanoscale dimensions.

In this paper, we present the methodology developed to characterize strain and crystallinity in both strained SiGe FinFET structures and FinFET structures with epitaxial embedded SiGe (eSiGe). We compare 2 complementary techniques used for characterization of strain on 3D fins. High Resolution X-ray Diffraction techniques with a spot size and a spatial resolution of 50 to 200 microns are non-destructive and the signal (averaged over many fins) is sensitive to defectivity, strain and Ge content. On the other hand, Transmission Electron Microscopy (spot size 0.3 – 5nm) is a destructive technique, dependent on the lamella thickness, and gives localized information on a few fins.

All measurements were made on blanket and fin array pads on specially designed macros. For XRD measurements, strain was evaluated using peak position information from the XRD Reciprocal Space Maps collected both parallel and perpendicular to the fin arrays. Measurements show that the stress in the SiGe fins is uniaxial – the SiGe fins are fully strained along the direction of the fins. The SiGe is partially relaxed perpendicular to the fins – the amount of relaxation dependent on the %Ge and the height of the SiGe fins. Advanced TEM analytical techniques (Nano beam diffraction, Dark Field holography and Energy-dispersive X-ray spectroscopy) were used to map the strain and %Ge over the height and the width of the SiGe fins. There was good correlation between the average strain and %Ge as determined from the TEM and XRD techniques. Results of the measurements will be compared with theoretical modeling, which is used to quantify the triaxial stress tensor components based on the experimentally determined lattice parameter values.

The advent of new HRXRD tools with 1D detectors and high intensity sources enable these measurements to be made over a couple of hours. Since XRD techniques are non-destructive, we will also discuss how this methodology can be easily adapted as in-line metrology to monitor the change in strain with processing.

This work was performed by the Research and Development Alliance Teams at various IBM Research and Development Facilities.

11:40am **MC-TuM12 Strain Measurement using Electron Beam Techniques**, ***Jean-Luc Rouviere***, CEA-University Grenoble Alps, France, *N. Bernier,* CEA, LETI, MINATEC Campus, France, *D. Cooper*, CEA-LETI, France **INVITED**

Strain can modify deeply material properties such as optical emission, transport properties or structural strength. With the development of nanotechnologies, the need of tools that can measure strain with high accuracy (about 0.01%) and high spatial resolution (about 1 nm) has appeared. The demand of Microelectronics industry has been particularly strong since Intel has implemented strained channels to boost the transport performance of their devices, and during the last decade, many new TEM base techniques have been developed to reach these goals. Of course, not only the microelectronics industry, but also any fields involving nanomaterials will benefit from these developments.

In this presentation, after a short review of the different TEM techniques, we will focus on the solution we have developed and chosen: **Nanobeam Precession Electron Diffraction (N-PED)**. Like in all TEM diffraction techniques, a small electron beam is made and diffraction patterns are acquired at different positions of the electron beam. In addition, in N-PED, the incident electron beam is rotated by a small angle around the observation direction and a descan is applied after the sample in order to bring back the diffracted beams to their unprecessed positions. In fact there is a compromise between spot size, beam convergence and precession angle. We adopted a setting where the beam convergence is about 2.2 mrad, the probe diameter is of about 1 nm, and the precession angle is below 0.5°. The advantages of this setting for strain measurement are mainyfold : (i) the diffraction spots have disk shapes and do not saturate, (ii) the intensity within the diffraction disks is more uniform (iii) more diffraction disks are visible (iii) a greater accuracty is obtained by locating the edges of the disks, (iv) the measurements are very stable versus changes in sample thickness or orientation and (v) strain maps of 4 components of the 3D strain tensor can be obtained with one zone axis orientation. **We will show how this simple and robust N-PED technique has been used successfully for the analysis of microelectronics devices and nanostructures**. In our FEI TITAN ultimate microscope where we used a Gatan Ultrascan CCD camera, the main drawbacks of N-PED are (i) its relatively slow speed and (ii) the amount of stored data to acquire large maps. For instance, to acquire 100x50 diffraction patterns containing 1Kx1K pixels, it took 90 minutes and 12 Gbytes on the hard disk. However with the new available fast cameras and larger disks, these issues are greatly reduced.

Magnetic Interfaces and Nanostructures
Room: 230A - Session MI-TuM

Oxides, Fluorides, and Spin Structures
Moderator: Greg Szulczewski, The University of Alabama

8:00am **MI-TuM1 Magnetic Interactions at Perovskite Oxide Interfaces**, ***Yayoi Takamura***, *B. Li, R.V. Chopdekar,* University of California, Davis, *E. Arenholz,* Lawrence Berkeley National Laboratory, *A. Mehta,* SLAC National Accelerator Laboratory, *M.D. Biegalski, H.M. Christen*, Oak Ridge National Laboratory **INVITED**

Perovskite-structured oxides possess a wide range of intriguing and technologically relevant functional properties including ferromagnetism, ferroelectricity, and superconductivity. Furthermore, the interfaces of perovskite oxides have been shown to exhibit unexpected functional properties not found in the constituent materials. These functional properties arise due to various structural and chemical changes as well as electronic and/or magnetic interactions occurring over nanometer length scales at the interfaces, and they have the potential to be harnessed to enable new, more versatile, and energy efficient devices. In particular, magnetic exchange coupling at ferromagnetic/ antiferromagnetic (FM/AFM) and FM/FM interfaces are crucial due to their applications in magnetic technologies such as magnetic read heads and nanostructured permanent magnets. In this talk, we report on a unique spin-flop coupling observed at FM La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO)/AFM La$_{0.7}$Sr$_{0.3}$FeO$_3$ (LSFO) interfaces and contrast these interfaces to FM/FM interfaces consisting of hard FM La$_{0.7}$Sr$_{0.3}$CoO$_3$ (LSCO) and soft FM LSMO where exchange-spring behavior has been observed. Detailed structural and magnetic characterization of the individual layers was carried out using a combination of resonant x-ray reflectometry and element-specific soft x-ray magnetic spectroscopy, which provide more insight into interfacial effects over conventional characterization techniques such as bulk magnetometry. Our results indicate that the complex interplay between the charge, lattice, spin and orbital degrees of freedom at perovskite oxide interfaces provides a versatile route to control magnetic switching behavior as required for advanced magnetic device applications.

8:40am **MI-TuM3 X-ray Imaging of Magnetism at the Nanoscale**, ***Stefano Bonetti***, Stockholm University, Sweden, *R. Kukreja, Z. Chen,* Stanford University, *F. Macia, J.M. Hernandez,* Universitat de Barcelona, Spain, *A. Eklund,* KTH Royal Institute of Technology, Sweden, *D. Backes,* New York University, *J. Frisch,* SLAC National Accelerator Laboratory, *Y. Acremann,* Laboratorium für Festkörperphysik, ETH Zürich, Switzerland, *J. Katine,* HGST, *G. Malm,* KTH Royal Institute of Technology, Sweden, *S. Urazhdin,* Emory University, *A.D. Kent,* New York University, *Ohldag, J. Stöhr, H.A. Dürr*, SLAC National Accelerator Laboratory **INVITED**

In this talk, I will describe the new scanning x-ray transmission microscope instrument that we recently built at the Stanford Synchrotron Radiation Lightsource (SSRL), at the SLAC National Accelerator Laboratory. In a single experiment, we are now able to measure extremely small magnetic, elemental and chemical signals at the nanoscale (with 35 nm resolution), in buried layers. We can also achieve a temporal resolutions of 50 ps, and synchronize our instrument to a microwave generator in order to detect excitations of up to 10 GHz in frequency. In order to show the capabilities of our technique, I will present two of our most recent results.

At first, I will discuss our successful attempt to directly image the injection of spins from a thin film ferromagnet into a non-magnetic Cu layer, when a bias current is fed through the ferromagnet/non-magnet interface. The elemental and chemical specificity of x-rays allows us to distinguish spin accumulation on Cu atoms located at the interface from those within the bulk of the Cu film. Spin accumulation in the film gives rise to an average transient magnetic moment per Cu atom of 3×10^{-5} μ_B around the Fermi level, which we explain using Mott's two current model. We also find a greatly enhanced transient moment on the Cu interface atoms, which we attribute to enhanced spin dependent scattering via localized interface states.

Then, I will present the first time-resolved x-ray images of the spin-wave soliton generated by spin-torque when a spin-polarized current is injected from a nano-contact into an extended magnetic layer, a 5-nm thick permalloy (Ni$_{80}$Fe$_{20}$) film. The circular polarization of the photons, tuned at the resonant L_3 absorption edge of Ni, allows for selectively probing the dynamics of the magnetization in the film. By synchronizing the spin waves oscillations to the RF cavity of the synchrotron, we are able to create a phase resolved map of the magnetic excitation, i.e. a spin-wave "movie." The unprecedented combined temporal and spatial resolution, and the ability to look through the thick metal electrodes that provide the current necessary to excite the dynamics, reveal intriguing details of the spin-wave dynamics. In particular, we observe the emergence of a novel localized spin-wave soliton with a nodal line, i.e. with *p*-like symmetry, qualitatively different from the predicted solitonic excitation with essentially cylindrical symmetry (i.e. *s*-like).

Our studies provide a deeper understanding of magnetism at the nanoscale, and highlight the importance of nanoscale time-resolved techniques to tackle the challenges of modern magnetism.

9:20am **MI-TuM5 Complex Fluorides: A New Class of Multiferroic and Magnetoelectric Materials**, ***David Lederman**, A. KC, T.A. Johnson, C. Cen, A.H. Romero, P. Borisov*, West Virginia University **INVITED**

Transition metal fluoride antiferromagnets have been used to study the fundamental properties of exchange bias and magnetism at the interface between antiferromagnets and ferromagnets. The highly ionic nature of these compounds makes them ideal candidates for studying fundamental magnetic properties. Less studied are multiferroic fluoride compounds such as the orthorhombic $BaMF_4$ or the perovskite $NaMF_3$ materials, where M is a transition metal. Recent theoretical and computational work has suggested that the some of the $BaMF_4$ compounds should be magnetoelectric and that the perovskite fluoride compounds in particular should have large canting of the antiferromagnetic structure which results in strong weak ferromagnetism. In this talk I will describe recent work in the growth of thin films of these materials using molecular beam epitaxy. Their magnetic properties were measured using SQUID magnetometry and their ferroelectric properties were measured using scanning probe microscopy and direct ferroelectric polarization measurements. For the $BaMF_4$ compounds, we were able to confirm that the Ni and Co compounds are multiferroic, while the Fe compound is definitely not multiferroic. I will also discuss the growth of $NaMnF_3$ thin films and their magnetic and dielectric properties as a function of temperature and magnetic fields.

11:00am **MI-TuM10 Spin-Dependent Size of Interband Hybridization Gap: The Interplay of Adlayer and Substrate States in Pb/Cu(111)**, ***Markus Donath**, S.N.P. Wissing, K.T. Ritter, A.B. Schmidt, P. Krueger*, Muenster University, Germany

In view of spintronics applications, spin-polarized valleys are a key issue to realize spin-polarized currents. To date, spin-polarized valleys have been discovered in surface states at high-symmetry points in momentum space (see, e.g., [1]). We propose and have discovered an alternative way of producing spin-polarized valleys via hybridization gaps induced by spin-orbit interaction. So far, spin-orbit-influenced hybridization led to spin-dependent avoided band crossings, yet with no energy gap of spin-dependent size, i.e., no spin-polarized valleys.

We investigated the unoccupied electronic structure of Pb/Cu(111) by spin- and angle-resolved inverse photoemission. In these studies, we discovered a hybridization gap with spin-dependent size, about 200 meV for the one and even larger than 500 meV for the other spin direction, although not in a fundamental band gap at the Fermi level. Yet more importantly, we revealed the mechanism behind the formation of this spin-dependent valley-like gap structure by a tight-binding model based on *ab initio* calculations: The way of how adlayer and substrate states interact [2].

[1] K. Sakamoto et al., Nat. Commun. **4**, 2073 (2013).

[2] S.N.P. Wissing et al., Phys. Rev. B (Rapid Communications), accepted (2015).

11:20am **MI-TuM11 Energy Dispersion and Spin Structure of Unoccupied Electronic States of BiTeI: A Matter of Surface Termination?**, ***Christian Langenkämper****, *K. Miyamoto, A.B. Schmidt, P. Krüger, M. Donath*, Westfälische Wilhelms-Universität Münster, Germany

Recently, a new class of “Rashba materials” has been discovered: Non-centrosymmetric materials like MoS_2 [1] and BiTeI [2] show a lifting of the spin degeneracy in the electronic structure due to the bulk Rashba effect. So far, studies on BiTeI are limited to the occupied band regime and its Rashba-type spin dependence. For future applications, e.g. opto-spintronics, a substantiated knowledge about the complete spin-dependent electronic structure, occupied as well as unoccupied, is needed.

We present a combined experimental and theoretical study on the unoccupied electronic structure of BiTeI along the Γ-K direction. In our spin-resolved inverse photoemission measurements, we found a strong influence of the sample quality on the energy dispersion around the Γ point. Based on band structure calculations, we attribute this effect to different surface terminations, Te or I. Due to band bending, the different terminations have a direct consequence for the band dispersion. This effect is not observed at K, where the spectra do not depend on the surface quality. We will discuss this result in the context of *ab initio* band structure calculations. - In addition, we studied the spin structure of the bands along Γ-K. Around the Γ point, we found in-plane spin polarization in agreement with previous photoemission experiments for the occupied states [2]. Upon approaching K, the direction of the spin polarization rotates from in-plane to fully out-of-plane in accordance with the crystal symmetry.

[1] Suzuki *et al*., Nature Nanotechnology **9**, 611 (2014)

[2] Ishizaka *et al*., Nature Materials **10**, 521 (2011)

11:40am **MI-TuM12 Abnormal Asymmetric Domain Expansion and Skyrmion Bubble Stability in Thin Films with Strong Dzyaloshinskii-Moriya Interaction**, ***Lucas Caretta**, M. Mann, AJ. Tan, G.S.D. Beach*, Massachusetts Institute of Technology

The Dzyaloshinskii-Moriya interaction (DMI) at heavy-metal/ferromagnet interfaces can stabilize chiral spin textures [1]. It has recently been shown that field-driven bubble domain expansion in perpendicularly-magnetized thin films is asymmetric under the application of an in-plane field, which can be used to quantify the DMI effective field in the domain wall (DW) [2]. We have imaged domain expansion in Pt(3nm)/Co(0.9nm)/Pt(x)/GdOx(3nm) films using wide-field Kerr microscopy to characterize this behavior systematically as a function of DMI strength. In the case of null or weak DMI, realized when top and bottom Pt layers are of similar thickness, the in-plane field dependence of the DW velocity is well-described by the simple expansion model derived in Ref. [2]. However, in the case of strong DMI, we find a strongly nonmonotonic behavior due to flattening of the DW, minimizing Zeeman energy and DMI energy. Moreover, we show that when the ratio of the DMI effective field to the perpendicular anisotropy field is large, expanding bubble domains leave behind fine-scale dendritic structures, consisting of coupled 360 degree DWs. These dendritic structures can be manipulated to form stable skyrmion bubbles. We show that the stability of skyrmion bubbles is a strong function of the applied in-plane field near the DMI field. The skyrmion bubble annihilation field becomes deterministic at large in-plane fields.

1. A. Fert et al., Nat. Nano., 8, 152-156 (2013)

2. S.G. Je et al., PRB 88, 214401 (2013)

12:00pm **MI-TuM13 Control and Characterization of Magnetic Domain Patterns in Complex Oxide Microstructures**, ***Michael Lee**, T. Wynn, R.V. Chopdekar*, University of California, Davis, *E. Folven, J. Grepstad*, Norwegian University of Science and Technology, *A. Scholl, A. Young*, Lawrence Berkeley National Laboratory (LBNL), *S. Retterer*, Oak Ridge National Laboratory, *Y. Jia, B. Li, Y. Takamura*, University of California, Davis

Future memory devices must achieve improved storage density, stability, and low power consumption. To this end $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) is a promising material due to the confluence of many scientifically interesting functional properties, including ferromagnetism, colossal magnetoresistance, and high spin-polarization. The ability to tune these properties through a number of different stimuli is equally encouraging. In order to utilize LSMO the magnetic behavior of nanostructures must be well characterized, but due to the vast array of energetically competitive interactions present, size effects play a significant role in oxide nanostructures.

In this work we investigated the evolution of domain structure as a function of temperature in micromagnets patterned into epitaxial films of LSMO via x-ray photoemission electron microscopy (XPEEM). Results showed transitions from vortex to Landau patterns in circular patterns (2µm in diameter) indicating that saturation magnetization and magnetocrystalline anisotropy (K_1) have different dependence on temperature. Additionally, squares (also 2µm) with edges aligned along the hard magnetization axis began in the Landau state dictated by shape anisotropy, but developed distinct inner and outer flux closure structures as K_1 becomes stronger at lower temperatures. This could mean the creation of magnetic domain structures in devices that have more fine-tuned and efficient behavior. The presence of these novel spin-textures has been used to extract approximate fundamental magnetic parameters for LSMO at micro- and nano-dimensions. We have developed a method to extract values of K_1 from simulations of the observed XPEEM images. Parameters obtained from circular micromagnets were used to simulate other experimentally observed magnetic domain structures and confirm the validity of the procedure. This is a new analysis technique making it possible to locally measure magnetic

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*** Falicov Student Award Finalist**

properties in structures that would otherwise be difficult or impossible to characterize.

Novel spin-textures have been observed as a direct result of studying materials systems that express magnetocrystalline anisotropy. Using the newly developed technique, approximate values of magnetocrystalline anisotropy have been uncovered for the micromagnets studied to more clearly describe the magnetic behavior of LSMO nanostructures. The outcome of this project will improve the quality of future research due to a deeper understanding of the delicate balance of energies.

MEMS and NEMS
Room: 211A - Session MN+MG-TuM

Multiscale Phenomena & Interactions in Micro- and Nano-Systems (8:00-10:00 am) & Optical MEMS/NEMS, Photonics, and Quantum Nanosystems (11:00 am-12:20 pm)

Moderator: Robert Davis, Brigham Young University, Robert Ilic, National Institute of Standards and Technology (NIST), Meredith Metzler, University of Pennsylvania

8:00am **MN+MG-TuM1 Microengineering for Mechanobiology**, ***Beth L. Pruitt***, Stanford University **INVITED**

Living organisms generate and respond to mechanical forces and these forces are sensed and created by specialized cells in the body. Force generation and sensing, or more broadly the mechanobiology coupling tissue (cell) mechanics and biology, are essential in normal development, wound healing, and tissue homeostasis. Our mechanical senses of hearing and touch allow us to navigate our environment and interact with one another, yet they remain the least understood of our perceptive senses. Basic life sustaining functions such as breathing, circulation, and digestion are driven autonomously by coordinated contraction of specialized muscle cells, yet how these functions incorporate active feedback via force sensing at the cellular level is an area of active study. Meanwhile, a variety of specialized stretch activated receptors and mechanically mediated biochemical signaling pathways have been identified in recent years. Importantly, defects in proteins of these mechanically mediated pathways and receptors have been implicated in disease states spanning cardiovascular disease, cancer growth and metastasis, neuropathy, and deafness. Thus, understanding the mechanical basis of homeostasis (health) and defective cell renewal function (disease) increasingly requires us to consider the role of mechanics. To study how cells and tissues integrate mechanical signals, we and others have developed specialized cell cultures systems and micromachined tools to stimulate and measure forces and displacements at the scale of proteins and cells. A key feature of such experiments is the ability to observe cell outputs such as morphological changes, protein expression, electrophysiological signaling, force generation and transcriptional activity in response to mechanical stimuli.

8:40am **MN+MG-TuM3 Introducing Students to MEMS: A Practical Process for the Fabrication and Testing of Piezoresistive Cantilevers**, ***Frederic Loizeau***, *E. Sadeghipour, T. Larsen, J.Y. Sim, C. Roozeboom, E. Mazzochette, B.L. Pruitt*, Stanford University

We present a laboratory course to introduce students to Micro-Electro-Mechanical Systems (MEMS) through fabrication and characterization of piezoresistive cantilevers. We developed a process flow comprised of only three photolithography steps to minimize time spent by the students in the cleanroom and workload of the teaching team. Students performed hands-on work on over 80% of the fabrication process and thus earned qualification status to operate the standard tools in our cleanroom. The course included practical experience with signal conditioning, noise, and sensitivity measurements. The lab component spanned six sessions of 4.5 hours each and is ideal for integration in a lecture course or a two-week standalone mini-course.

The hands-on laboratory component was paired with lectures covering cleanliness, process selection, and device design and characterization. Six lab sessions of 4.5 hours each covered the fabrication and characterization of piezoresistive cantilevers. In each session, teams of five students learned fundamental MEMS processes and equipment use while fabricating pre-designed devices. Weekly homework reinforced design, process, and testing concepts, e.g., predicting device performance, completing lithography steps, or building a measurement circuit. Device fabrication was completed in the first four lab sessions. Modest process support was provided outside of class by the teaching team for batch processes such as wafer preparation, metallization, and final HF release. The yield of the fabrication process was >90%. Each team built their own Wheatstone bridge and amplifier circuit to readout the piezoresistor signal prior to lab sessions 5 and 6 for device characterization. In session 5 they learned to use a dynamic signal analyzer to measure the Hooge and Johnson noise. In session 6, the students measured the power spectral density of cantilever tip deflection due to thermomechanical noise using a laser-Doppler vibrometer (LDV). From these measurements, they estimated the spring constants, resonant frequencies and quality factors of the cantilevers. Using a piezoelectric shaker and the LDV, students simultaneously measured the cantilever deflection and the piezoresistor bridge output and then used this to calculate cantilever sensitivity and resolution. Finally, experimental measurements were compared with theoretical predictions.

9:00am **MN+MG-TuM4 Deflection Control of an Electroactive Polymer Bimorph Actuator by Carrier Frequency Modulation**, ***Leeya Engel***, Tel Aviv University, Israel, *K. Van Volkinburg,* University of California Irvine, *Y. Shacham-Diamand,* Tel Aviv University, Israel, *G.N. Washington,* University of California Irvine, *S. Krylov*, Tel Aviv University, Israel

In microelectromechanical systems (MEMS), actuator deflections are typically controlled by varying the voltage used to drive the active element. In this work, we use the frequency sensitivity of the permittivity of relaxor ferroelectric polymer poly(vinylidene fluoride-trifluoroethylene chlorotrifluoroethylene (P(VDF-TrFE-CTFE)) as an additional parameter for controlling the deflections of an electroactive polymer bimorph actuator.

The amplitude of the tip deflection of the electroactive polymer bimorph actuator, whose active layer comprised a thin film of P(VDF-TrFE-CFE), increased with the voltage applied at constant frequency, as expected. When the peak-to-peak displacements of the beam were plotted as a function of frequency at constant peak-to-peak voltage, a nonlinear decrease in tip deflection with increasing frequency was observed, independent of the resonance of the device. Electrical characterization of the material shows that the real component of the permittivity is ~55.5 at 100 Hz, but at radio frequencies, it decreases to 4. Dielectric losses are high at frequencies on the order of kHz–GHz with a coefficient of loss above 60% around MHz frequencies. Thus, the decrease in magnitude of electromechanical displacement with frequency can be attributed to the decrease in the permittivity-dependent electric field related electrostrictive coefficient with frequency. Deflections were recorded using both a laser Doppler vibrometer (LDV) and by interpreting the potential difference that formed across an integrated layer of piezoelectric polymer PVDF during actuation. In addition to adding mechanical sensing capabilities to the device, the PVDF layer also functioned as the passive layer of the bimorph structure.

This work directly demonstrates the dependence of the electromechanical behavior of an electroactive polymer actuator on the dielectric properties of P(VDF–TrFE–CFE) and our ability to exploit that dependence for an additional control parameter of the device. Frequency modulation of polymer beam deflections and integration of sensing capabilities can benefit the developing field of polymer microactuators, in applications such as "smart" prosthetics and implants, targeted drug delivery, tools for less invasive surgery, microfluidics, and on-chip cooling.

9:20am **MN+MG-TuM5 Solder Based Self-Assembly Method For 3D Integration Using Poly-Acrylic Acid**, ***Connor Smith***, *Y. Feng, S.L. Burkett*, The University of Alabama

The use of Solder Based Self-Assembly (SBSA) in fabricating 3D structures on the microscopic scale is a process with numerous potential applications. This method involves creating copper plated 2D flat patterns of various shapes on a silicon substrate. Then, upon dip soldering these patterns and re-flowing the solder with hydrochloric acid, surface tension pulls up on these shapes to form a 3D structure. However, the use of a SiO2 sacrificial layer in performing this method results in the need for hydrofluoric acid (HF) during the etching phases, which has many dangerous hazards associated with it. The goal of this research is to develop a new process in which a water-soluble polymer, poly-acrylic acid (PAA), may be used as a sacrificial layer instead of SiO2--thus making the micro-fabrication process much safer. By working through the original SBSA method, and overcoming the various obstacles created by needing to protect the PAA from being exposed to water earlier than desired, an effective procedure has been developed. Through completing this project, future attempts to fabricate microscopic 3D structures using the SBSA method will be safer and less prone to dangerous HF exposure. Furthermore, removing HF etching from the procedure will reduce the time required to move through the process as a whole, thus increasing its efficiency.

11:00am **MN+MG-TuM10 Mechanics and Spins in Diamond**, *A. Bleszynski Jayich, **Donghun Lee***, University of California at Santa Barbara **INVITED**

Single crystal diamond mechanical resonators have recently emerged as a promising platform for hybrid quantum systems comprising spins and phonons. Diamond mechanical resonators exhibit exceptionally high quality factors[1] and diamond plays host to a highly coherent spin system: the nitrogen vacancy (NV) center. The NV center is an atom-sized defect in diamond that is a remarkably good sensor of magnetic, electric, thermal, and strain fields on the nanoscale. Because of its strain sensitivity, the NV can be easily coupled to a mechanical degree of freedom. We have recently characterized the sensitivity of the NV's ground state spin to strain by controllably applying dynamical strain to NV centers embedded inside high quality factor diamond mechanical resonators[2]. We have also recently demonstrated strain-mediated coupling to the optical transitions of single NV centers. Through strain coupling, we show that coherent mechanical control of individual spins in diamond is possible. These results are encouraging for proposals to use such a spin-mechanical platform for spin-squeezing, phonon-mediated spin-spin interactions[3], and phonon cooling of macroscopic mechanical resonators[4]. We discuss the necessary steps needed to reach these goals and current progress including improvements in diamond fabrication, NV formation, and readout techniques.

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2. Ovartchaiyapong, P., Lee, K. W., Myers, B. A. & Jayich, A. C. B. Dynamic strain-mediated coupling of a single diamond spin to a mechanical resonator. *Nat Comms* **5,** (2014).

3. Bennett, S. *et al.* Phonon-Induced Spin-Spin Interactions in Diamond Nanostructures: Application to Spin Squeezing. *Physical review letters* **110,** 156402 (2013).

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11:40am **MN+MG-TuM12 Nano-Optomechanical Fin Resonators Designed for Sensing in Liquid Environments**, ***Jocelyn Westwood-Bachman****, W.K. Hiebert*, University of Alberta and The National Institute for Nanotechnology, Canada

Nanomechanical systems are well known for their mass sensitivity, and are often used as mass sensors [1]. However, nanomechanical sensors tend to operate poorly in liquid environments due to viscous damping by the surrounding fluid. This drawback is particularly challenging for biological and related clinical sensing applications, where it is ideal to detect molecules within a liquid environment [2]. Here, we show the design of a fin-like nanomechanical resonator specifically for use in liquid environments. This design features a cantilever pointing out of the plane of the silicon device layer. This is in contrast to typical cantilevers that are in the silicon plane. The length of the cantilever is determined by the thickness of the silicon layer used, and the thickness of the resonator is designed to achieve specific resonance frequencies. The motion of these fin-like resonators is read out by an adjacent photonic microring resonator [3]. This microring resonator also provides an avenue for optical actuation of the fin resonator. The benefit of this design over existing designs is twofold. Firstly, our integrated photonics detection and actuation scheme provides higher displacement sensitivity than interferometric techniques [4]. Secondly, the fin is designed to operate at high frequencies (above 500 MHz) but can still have comparable surface area to nanoscale cantilevers as the width can be made arbitrarily large. This increases the sensing area while reducing the overall dissipation [5]. We will illustrate our design methodology and show the first generation of devices. As the as-fabricated devices have larger-than-desired feature sizes due to the limitations of photolithography, we will also discuss potential methods of tuning the device size post-fabrication. Specifically, we explore the possibility of trimming the fin resonator using Ga and He ion milling.

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12:00pm **MN+MG-TuM13 Directed Magnetic Optical Resonator Microballoons for Particle Imaging Manometry in 3D Environment**, ***Niladri Banerjee***, University of Utah

Measurement of velocity and pressure field in microfluidic 3D environment is vital in complete characterization of any fluid flow for capillary networks, flow-based separators and microchips for different biological applications. Particle imaging velocimetry though is the gold standard for measuring in-flow velocity, there has been no equivalent technique to perform pressure mapping. Recently hollow spherical micro-particles were fabricated to perform pressure measurement inside microfluidic channels. But lack of control on the trajectory of these particles inside micro-channels resulted in the ability to perform on-the-fly in-flow pressure mapping by spectroscopic method at any arbitrary location.

In this paper, we present the design, fabrication and testing of engineered magnetic micro-balloon pressure sensor particles. These directed particles, when injected into the flow-stream of any microchip, can be localized at any specific location of interest for dynamic pressure measurement. Each particle consists of a vacuum sealed spherical cavity along with a gold-nickel-gold magnetic tail attached to a polymeric support stem. The hollow cavity sealed by a thin polymeric shell, behaving as a Fabry-Perot interferometer, changes in size due to external pressure variation, which is detected by spectroscopic technique. Moreover the magnetic tail enables temporary immobilization of these particles at any position in the channel by the application of external magnetic field. The fabrication of these particles is based on buried sphere technology (BST). The fabrication starts with patterning of circular holes on thermally oxidized silicon. A trench 10-15 µm deep into the substrate is etched by DRIE. Next we oxidize the sample to grow 100 nm of oxide in order to protect the sidewalls of the trench. On selectively etching oxide from trench-bottom wall, spherical cavity of 6 µm radius is etched by XeF_2. Then the spherical cavity is smoothened and hole necked down by subsequent oxidation and poly-deposition process steps. Al_2O_3 is then deposited by ALD forming a gas leakage-stop layer followed by parylene-C, to form the micro-balloon wall. Then a gold-nickel-gold (0.2-0.5-0.2 µm) sandwich is sputtered and encapsulated using another 1 µm layer of parylene-C. Real-time in-flow pressure measurement using 0.1T permanent magnet is performed at 8 magnet-specified locations with particles dispersed in IPA inside a serpentine test-chip. Spectral reflectance measurement indicates a pressure sensitivity of 37nm/psi. The paper will discuss the fabrication and test of the magnetic particles in detail with additional internal pressure measurement examples.

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.

Work at Lawrence Livermore National Laboratory was performed under the auspices of the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering for FWP SCW0974 under Contract DE-AC52-07NA27344. Work at the University of Tennessee was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering. Research conducted at the Center for Nanophase Materials Sciences is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division of the U.S. Department of Energy, Office of Science, Office of Basic Energy Science.

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.

References

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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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2 Titov, V. M., Tolochko, B. P., Ten, K. A., Lukyanchikov, L. A. & Pruuel, E. R. Where and when are nanodiamonds formed under explosion? *Diamond and Related Materials***16**, 2009-2013, doi:10.1016/j.diamond.2007.09.001 (2007).

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 $\sim 4x10^7$ 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 ($MeCpPtMe_3$) 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 $MeCpPtMe_3$ and dry air (20% wt. O_2), 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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Plasma Science and Technology
Room: 210A - Session PS+BI+SM-TuM

Plasmas for Medicine and Biological Applications
Moderator: Satoshi Hamaguchi, Osaka University, Japan

8:00am **PS+BI+SM-TuM1 Glow-Discharge Plasma Applications in the Biomedical Sciences: Frontiers and Horizons**, ***Buddy D. Ratner***, University of Washington **INVITED**

Plasma treatments for biomedical applications have been explored since the early 1960's, possibly earlier than that. Plasma treatments for medical devices and for materials used in biotechnology are now widely used and have improved he performance and safety of many devices. A few advanced technologies for biomedicine exploiting plasma deposition of organic thin films will be described. These include non-fouling surfaces, thermally responsive surfaces, biodegradable surfaces, rate-limiting barriers for controlled release and surfaces that permit the growth of precision polymeric brushes by atom transfer radical polymerization (ATRP). Frontiers for plasma deposition include better control of deposition chemistry, strategies to deposit unusual chemistries and depositions that integrate biological molecules and plasma-deposited chemistries.

8:40am **PS+BI+SM-TuM3 Non-Equilibrium Plasmas in Contact with Solutions: Biological Interactions and Material Synthesis**, ***Peter Bruggeman***, University of Minnesota **INVITED**

Non-equilibrium atmospheric pressure plasmas interacting with liquids offer a unique source of highly reactive chemistry beneficial for many applications in biology, medicine and advanced materials manufacturing. It has been shown that these plasma-liquid interactions can lead to inactivation of bacteria and virus and the synthesis of nanoparticles. Nonetheless the underpinning mechanisms are at least poorly understood. My group has been strongly involved in the study of the reactive chemistry of a well-characterized RF driven atmospheric pressure plasma jet and its interaction with liquids.

The presentation will highlight some examples of reaction pathways responsible for the inactivation of bacteria and virus in solution and the synthesis of silver nanoparticles from $AgNO_3$ solutions. I will illustrate the importance of reactive plasma chemistry induced by neutral gas phase reactive species such as OH, H_2O_2 NO, O, H, O_3 and singlet oxygen. In addition, we will show that UV emission, which is often neglected as a possible mechanism, can be important in some cases.

9:20am **PS+BI+SM-TuM5 Plasma Biomedicine and Reactive Species**, ***David Graves***, University of California at Berkeley **INVITED**

Low temperature plasma research directed towards biomedical applications such as sterilization, surgery, wound healing and anti-cancer therapy has seen remarkable growth in the last 3-5 years, but the mechanisms responsible for the biomedical effects have remained mysterious. It is known that CAP readily create reactive oxygen species (ROS) and reactive nitrogen species (RNS). Other potentially important plasma-generated species effects include charges, fields and photons. ROS and RNS (or RONS), in addition to a suite of other radical and non-radical reactive species, are essential actors in an important sub-field of aerobic biology termed 'redox' (or oxidation-reduction) biology. I will review the evidence suggesting that RONS generated by plasmas are responsible for their observed therapeutic effects. In addition, I will present several ideas about the most likely biological response mechanisms that are likely involved in therapeutic plasma biomedicine.

11:00am **PS+BI+SM-TuM10 Cold Atmospheric Plasma for the Treatment of Chronic Infected Wounds**, ***Jennifer Granick***, *V.S.S.K. Kondeti, A. Truong, R.C. Hunter, P.J. Bruggeman*, University of Minnesota

Two percent of the US population suffers from chronic non-healing wounds, often complicated by antibiotic-resistant bacterial infections, and the staggering cost of wound care exceeds $50 billion per year. Of increasing concern are multi-drug resistant bacteria, including methicillin-resistant *Staphylococcus aureus* and multi-drug resistant *Pseudomonas aeruginosa* infections. Within wounds, these bacteria adopt a biofilm-like state, and become notoriously recalcitrant to conventional antibiotic therapies. Currently approved products for the treatment of chronic wounds have not proven to be a panacea due to the complex nature of wound healing.

The ideal therapy for chronic, infected wounds would be non-painful, bactericidal without risk of resistance, able to break-up biofilms and enhance wound healing. Recently, there has been interest in the use of cold atmospheric plasma (CAP) technology for the treatment of infections and non-healing wounds. The technology could potentially fulfill the requirements of an ideal wound healing therapy. CAP devices producing ionized gas have been developed that can operate in ambient air and that are safe to touch without any pain sensation. CAP generates a complex mixture of reactive oxygen and nitrogen species (RONS) that are able to kill bacteria, while stimulating host cell growth. CAP has the potential to combine antiseptic and wound healing capabilities in a single treatment procedure and could eliminate the risk of cytotoxicity present in many current treatment methodologies for infected wounds.

The effects of CAP on bacteria and mammalian keratinocytes and fibroblast cells have been evaluated *in vitro*. Our prototype argon CAP device produces antibacterial effects on planktonic bacterial cultures of *S. aureus* and *P. aeruginosa* at a maximal treatment duration of 20 ml/min at conditions that do not impact cell viability of fibroblasts and keratinocytes *in vitro*. We have also recently demonstrated that CAP is effective in reducing the viability of *P. aeruginosa* biofilms grown *in vitro*. When grown on the surfaces of PVC microtitre plates for 48 h, argon-air derived CAP treatment of established biofilms showed a 95% reduction in cell viability, as determined by resazurin fluorescence, relative to untreated controls, when treated at a dose of 30min/ml, which is similar to the treatment time equivalent of mammalian cell treatment.

As part of the early investigations of the use of CAP treatment as a viable therapy for chronic-infected wounds, the presentation will focus on bacterial biofilm reduction by CAP treatment *in vitro* as well as in a mouse skin wound model. The effects on mouse host cells will be examined.

11:20am **PS+BI+SM-TuM11 Humidity Effect on the Surface Modification and Bio-Deactivation of Lipopolysaccharide (LPS) by Surface Micro-Discharge (SMD)**, ***Pingshan Luan***, *E.A.J. Bartis, A.J. Knoll*, University of Maryland, College Park, *C. Anderson, D.B. Graves*, University of California at Berkeley, *J. Seog, G.S. Oehrlein*, University of Maryland, College Park

The surface micro-discharge (SMD), due to its scalable large area and flexibility of working gases, has great potential for many applications such as material processing and plasma medicine. The SMD normally works under ambient air conditions that contain not only N_2 and O_2 but also water vapor which can have a large impact on both the discharge behavior and plasma gas chemistry. In this study, we evaluate the effect of ambient humidity on SMD in various N_2/O_2 mixtures and the subsequent effect on the surface modification and bio-deactivation of lipopolysaccharide (LPS). Electrical behavior and optical emission spectrum (OES) of the SMD source were studied. We found that while the additional moisture did not help create strong OH (A-X) emission from SMD, it resulted in lower plasma density and extra power dissipation. We used X-ray photoelectron spectroscopy (XPS) to characterize the surface modification of LPS after treatment. We found that all SMD-treated LPS surfaces show oxygen uptake and formation of surface-bound NO_3, while the amount of these modifications was strongly dependent on the ambient gas composition. By comparing the XPS of wet-treated (50% relative humidity at 20 °C) surfaces with their dry counterparts, we find that the water vapor reduces both the oxygen uptake and surface NO_3 formation, and that the difference between wet- and dry-treated surfaces decreases with the increasing fraction of ambient N_2. When the N_2 fraction is up to 80% (synthetic air), the LPS surface shows comparable amount of modification with or without humidity. Among all the dry- and wet-N_2/O_2 mixtures, the dry 5% of N_2 ambient shows the greatest modification rate. We also evaluated the bio-deactivation efficiency of the SMD on LPS using enzyme-linked immunosorbent assay. Similar to surface modification, we found that the bio-deactivation rate of SMD in dry ambient is much higher than that of SMD in their wet counterparts, except the synthetic air condition which shows similar amount. The authors gratefully acknowledge financial support by the US Department of Energy (DE-SC0001939) and National Science Foundation (PHY-1004256 and PHY-1415353).

11:40am **PS+BI+SM-TuM12 Plasma Diagnostics of Dielectric Barrier Discharge within a Sealed Meat Package**, ***Vladimir Milosavljevic***, Dublin Institute of Technology, Ireland, *J. Lalor, P. Bourke, P.J. Cullen*, Dublin Institute of Technology

Atmospheric pressure, non-thermal plasma DBD is increasingly used in many processing applications. Despite their widespread usage, it remains largely unknown whether cold atmospheric plasma DBD maintains similar characteristics, such as gas temperatures and particle flux, when they breakdown while arcing or whether they possess different operating modes. It is essential for laboratory/industrial adoption of such plasmas that plasma diagnostics of the process are provided. Optical emission and absorption spectroscopy have been used as diagnostics techniques with an added avantage of their non-intrusive nature.

The type of operating gas influences the stability of atmospheric plasma discharges. In this study is used a sealed meat package filled with one of two gas mixtures: O_2-CO_2 and N_2-CO_2 . Different concentrations of nitrogen or oxygen and carbon-dioxide could cause the transition from a stable homogeneous discharge into a filamentary discharge. Atmospheric plasma discharges are affected by the surrounding ambient air, and for sealed packages from transfer between the package gas and the surrounding ambient atmosphere. In the vast majority of atmospheric plasma discharges, reactive nitrogen species dominates the ionic composition of atmospheric discharge and has an impact on the breakdown voltage. When N_2 is added/mixed with CO_2 plasma discharges, the CO_2 emission lines are significantly quenched. In the case of O_2-CO_2 chemistry, nitrogen is not a carrier gas but it still present in the package due to contaminant transfer with the surrounding ambient air, modifying the plasma chemistry in the package. The plasma's optical spectrum in O_2-CO_2 chemistry shows molecular oxygen, nitrogen and OH peaks. Oxygen could come from the ambient air, the O_2-CO_2 gas mixture or from humidity in the package. Electron impact excitation of molecular oxygen, at low collision energies, is of particular importance because of its role in atmospheric physics and has been objective of this study. In our study we have also recorded the O_3 band-head that belongs to the Hartley Band. Ozone plays very important role for the biological aspect of this study and shows the highest change in a concentration with the processing time. Combining the results from spectral radiation in the package provides an electron energy distribution function. The study includes a detailed experimental investigation of the spatial and temporal spectroscopic data and links them with plasma kinetics.

The research leading to these results has received funding from the European Union´s Seventh Framework Programme managed by REA

Research Executive Agency (FP7/2007-2013) under Grant Agreement number 605125.

12:00pm **PS+BI+SM-TuM13 Low-Temperature Plasma Surface Modification of Porous Polymeric Materials for Environmental and Medical Applications**, ***Michelle Mann***, *A. Pegalajar-Jurado, E.R. Fisher*, Colorado State University

Three-dimensional (3D) porous polymeric materials are widely used in biomedical and environmental applications, such as wound healing and water filtration. Polymers used for these applications are chosen for their mechanical properties and porosity, yet the surface properties, such as hydrophobicity, limit their use in aqueous environments. For example, polymeric ultrafiltration membranes typically require pretreatment before use and tend to foul due to adsorption of biomolecules in the watercourse. Bioresorbable polymeric scaffolds used for wound healing are prone to attachment of bacteria, leading to prolonged infection at the wound site. These issues can be addressed with two simultaneous approaches. To prevent bacterial attachment and proliferation, antibacterial properties can be introduced into the materials via incorporation of biocidal agents or antibacterial coatings. Moreover, surface modification can be used to create more compatible polymeric materials by increasing wettability. Through plasma processing, tailored surface modification can be achieved while retaining the morphology and bulk properties of the material. Here, we will describe the modification of ultrafiltration polysulfone (UPS) membranes and poly(ε-caprolactone) (PCL) scaffolds to create low-fouling materials with enhanced wettability. $H_2O_{(g)}$ plasma treatment of UPS membranes and PCL scaffolds results in materials with significantly enhanced wettability while scanning electron microscopy (SEM) images demonstrate porous morphology is maintained. X-ray photoelectron spectroscopy (XPS) data show an increase in surface oxygen content throughout the membrane cross-section after plasma treatment, and modified UPS membranes demonstrate a significant increase in initial water flux. In addition, the performance of modified UPS membranes in the filtration of biological solutions will also be discussed. Furthermore, the biological performance of PCL scaffolds incorporated with various biocidal agents will be presented along with biocidal agent leaching studies.

Plasma Science and Technology
Room: 210B - Session PS-TuM

Advanced BEOL/Interconnect Etching
Moderator: Tetsuya Tatsumi, Sony Corporation, Japan

8:00am **PS-TuM1 Interconnect Patterning in the EUV Era**, ***John Arnold***, IBM Research Division, Albany, NY **INVITED**

The semiconductor industry is currently passing through a pivotal moment as EUV lithography transitions from patterning research to industrial-scale integrated technology development. This change will have ramifications far beyond the lithography itself, including impacts on adjacent unit processes, process complexity, development and manufacturing cycle times, product cost, and product yield, quality, and reliability. The most direct and immediate changes will be in plasma etch, where the combination of new materials and new dimensions will drive significant new challenges – and opportunities. The timing of EUV's readiness for practical utilization is such that most of the initial applications will be at the wiring levels, both BEOL and MOL, and this presentation will focus on those. We will begin with an examination of EUV's placement in the overall technology roadmap and a review of the important differences between EUV and conventional lithography. The bulk of the presentation will be dedicated to applications for contact, local interconnect, and BEOL, with particular emphasis on lithography and especially etch process behavior and performance. A discussion of the operational ramifications of incorporating EUV into a mainstream technology development program will be followed by a brief consideration of the anticipated benefits for the final manufactured products. We will conclude with a critical comparison of EUV to 193nm-based multiple patterning approaches for the 7nm node.

This work was performed by the Research and Development Alliance Teams at various IBM Research and Development facilities.

8:40am **PS-TuM3 Challenges for the sub-32nm Pitch Self-aligned Quadruple Patterning (SAQP) at Back End of Line (BEOL)**, ***Nihar Mohanty***, *R. Farrell, A. Raley, E. Franke, J. Smith, S. Song, A. Ko, A. Ranjan, A. deVilliers, P. Biolsi*, TEL Technology Center, America, LLC, *W. Wang, G. Beique, C. Labelle, L. Sun, R. Kim*, Globalfoundries, Ny, Usa

Critical back end of line (BEOL) M_x patterning at 7nm technology node requires sub-36nm pitches necessitating the use of either extreme ultraviolet (EUV) lithography or 193nm-immersion-lithography based self-aligned quadruple patterning (SAQP). With enormous challenges being faced in getting EUV lithography ready for production, SAQP is expected to be the front up approach for M_x grid patterning for most of industry. In contrast to the front end of line (FEOL) fin patterning, which has successfully deployed SAQP approach since 10nm node technology, BEOL M_x SAQP is challenging owing to the required usage of significantly lower temperature budgets for film stack deposition. This has an adverse impact on the material properties of the as-deposited films leading to emergence of several challenges for etch including selectivity, uniformity and roughness.

In this presentation we will highlight those unique etch challenges associated with our BEOL Mx SAQP patterning strategy and summarize our efforts in optimizing the etch chemistries, process steps and plasma etch parameters for meeting the 7nm technology node targets. With the mandrel definition parameters being the most significant input function for final pattern performance, we will detail our efforts in improving the CD uniformity (CDU), profile and line edge roughness (LER) / line width roughness (LWR) for both the mandrel definition etches. All of the etch development for this work has been conducted in our dual frequency capacitively coupled plasma (CCP) chamber with optimized gap for good baseline uniformity and independent ion flux & energy control.

9:00am **PS-TuM4 Novel Patterning Process for the 7xnm and Beyond**, ***Toru Hisamatsu***, Tokyo Electron Miyagi Limited, Japan, *T. Oishi, S. Ogawa*, Tokyo Electron Miyagi Limited, *Y. Kihara, M. Honda*, Tokyo Electron Miyagi Limited, Japan

Multiple exposures with double (quadruple) patterning has been adopted due to recent advancements in miniaturization with mask patterning techniques, and as the technology continues to develop, EUV exposure will be used in the near future. Extending the current techniques into the next generation is approaching the limit to satisfy required fabrication specifications, as it is required to have fabrication control of less-than- a-nm-order.

In the patterning process, multilayer patterning with high accuracy to form a fine patterning is becoming critical, especially in regards to line-roughness (LER/LWR) reduction, pattern-size dependency reduction of ARDE origin, and selectivity enhancement of thin EUV-resist. Furthermore, patterning with universal CD shrinkage independent of the pattern types (hole, oval, L/S) is also being required.

To this date, challenges of precise CD controllability have been solved by combining DC-superimposed plasma which reduces line-roughness by its accelerated electron-beam to cure resist surface, followed by the Si coating effect and optimization of etch condition to form a protection layer on the surface[1,2]. However, it is evident that those current techniques will soon face the limit as the resist thickness is reduced with the employment of EUV exposure; therefore the breakthrough with the new approach is essential.

As a result of various feasibility studies put into effect for a problem solution of fine pattern formation, "fusion of ALD technology and etching" was confirmed to be very beneficial for its capability of atomic-level formation of surface protection film during the etch process. This technology enabled line-roughness reduction with pattern-size dependent CD shrink control, since the ALD step is used according to the optimum timing during the etch process, which forms proportional deposition on any type of patterns. This paper discusses the optimization of ALD step timing, its layer thickness and composition of corresponding etch flow, and introduces a possible solution to various patterning process issues without trade-offs. This technique enables atomic-level control during the etch process and thus, is promising for further miniaturization of the patterning process.

Reference

[1] M. Honda et al., AVS 60th Int. Symp. & Exhibit. (2013)

[2] M. Honda et al., Proc. of SPIE 8328-09 (2012)

9:20am **PS-TuM5 Advanced Interconnect Process Techniques with EUV Photolithographic Masks and Sub-50nm Pitch Structures**, ***Jessica Dechene***, *J.C. Shearer*, IBM Research Division, *A.P. Labonte*, GLOBALFOUNDRIES, *J. Lucas, H. Matsumoto, B. Messer, A. Metz*, TEL Technology Center, America, LLC, *C. Labelle*, GLOBALFOUNDRIES, *J.C. Arnold*, IBM Research Division

As the semiconductor industry moves into the sub-10nm technology nodes, feature pitches below 50nm become ubiquitous. To avoid the complications of SADP processing, EUV photolithography is being explored as a means to continue direct patterning. This brings forth etch processing challenges in three ways: First, EUV resists are thinner, softer and suffer from greater LER than 193nm optical resists. Second, the small dimensions and tight pitches are causing old problems, once thought of as solved, to reappear. Pattern collapse, aspect ratio dependent etching, ion deflection induced profile bowing, and feature induced CD variation are a few examples.

Third, new integrations seeking the use of self-alignment, including self-aligned etch are becoming more prevalent. These self-aligned methods at such small dimensions require innovated etch techniques in order to be enabled.

In this paper, we will discuss the theory behind the various process solutions used to solve these etch challenges. Bias pulsing was used to address aspect ratio dependent etching concerns, and gas pulsing was used to improve material and corner selectivity in a self align etch process. Dielectric etch process solution on a dual-frequency capacitively coupled plasma (CCP) system were applied to the EUV lithographic masks. Superimposing a negative DC voltage to control the emission of ballistic electrons along with chemistry balance was used to minimize feature-dependent etch CD bias. These innovative process options allowed for the development of dielectric RIE processes that hit target specifications in the demanding pitch and CD sizes generated by the EUV lithography.

This work was performed by the Research and Development Alliance Teams at various IBM Research and Development Facilities.

9:40am **PS-TuM6 Advanced Plasma Etch Techniques for Sub-50nm Pitch Contact & Interconnect Etches**, ***Andre Labonte***, Globalfoundries, NY, USA, *R. Chao, J.M. Dechene,* IBM Albany Nanotech Center, *B. Nagabhirava, P. Wang, P. Friddle,* Lam Research, *N. Rassoul,* ST Microelectronics, *C. Labelle,* Globalfoundries, NY, USA, *J.C. Arnold,* IBM Albany Nanotech Center, *M. Goss*, Lam Research

As the semiconductor industry drives into sub-50nm pitches, EUV patterning as well as SADP and SAQP techniques are being explored as means to achieve the desired CDs and pitches needed. EUV patterning is attractive for enabling direct patterning and in principle, is significantly less complicated than SADP, let alone SAQP. However, EUV patterning comes with its own set of challenges, such as softer and thinner resists relative to optical 193nm resists. Also, to date, EUV resists have exhibited more LER/LWR than optical 193nm resists. Finally, the smaller features and pitches are resulting in the reoccurrence of old scaling issues such as RIE lag and pattern collapse. Many of these challenges are being met with innovative plasma etch techniques.

In this paper we discuss the theory behind many of the techniques used to solve the afore mentioned challenges associated with EUV and sub-50nm pitch patterning. In particular, RF pulsing and Bias pulsing are used to increase EUV resist selectivity, reduce LER/LWR, avoid pattern collapse and improve RIE lag in the dielectric etch. In addition we will also discuss the theory and application of AMMP (Advanced mixed mode pulsing) to improve the corner selectivity of low-k spacer in MOL to allow for the generation of self-aligned contacts. Finally, AMMP techniques were used to mitigate feature to feature CD variation incoming from litho.

This work was performed by the Research Alliance Teams at various IBM Research and Development Facilities.

11:20am **PS-TuM11 Characterization of Patterned Porous Low-*k* Dielectrics after Plasma Patterning and Subsequent Wet Processing/Cleaning**, ***QuocToan Le***, *E. Kesters, S. Decoster, B.T. Chan, F. Holsteyns,* IMEC, Belgium, *S. De Gendt*, IMEC, KU Leuven Belgium

Porous dielectrics have been commonly used in micro- and nanotechnologies since the past decade. Their chemical composition and porous properties make them more susceptible to physical and chemical damage. In particular, pattern etching and subsequent processes for removal of resist layers and/or post-etch residues are critical steps that potentially modify the dielectric properties [1].

This study first focuses on the modification of the porous dielectric material (pore structure, surface sealing, wettability) using a patterned line/trench test structure of 45 nm ½ pitch (Fig. 1). Several methods were applied for characterization of the patterned structure used in this study, including ellipsometric porosimetry (EP), X-ray photoelectron spectroscopy (XPS), and Fourier transform Infrared spectroscopy (FTIR). Fig. 2 shows the variation of the polarization state, expressed here by Delta angle, as a function of the relative pressure of toluene (used as a probe for porosity change). For the 45 nm patterned structure, the rapid change in Delta angle reflects the adsorption of toluene into the porous network. This clearly indicates that the patterned low-k surface remained unsealed after the C_4F_8/CF_4-based etch plasma process. In contrast, the surface of the blanket low-k film was almost sealed, evidenced by a very slow and irreversible toluene adsorption. Note that the sealing layer is only concerned the surface. The approach and characterization methods utilized for determination of the sealing thickness and the internal hydrophobic/hydrophilic properties [2] of the patterned porous low-k structures will be discussed.

Another aspect of this study concerns the surface composition of the patterned feature, type of the residues generated during the plasma etch, and the effect of a subsequent wet clean step. The latter is usually required before the deposition of the barrier layer. Substantial amount of fluorinated etch residues were detected on both the TiN surface and the dielectric sidewall and bottom. As shown in Fig. 3, the XPS F 1s core-level spectrum for the surface after the OSG etch consisted of two main components: the peak centered at ~684.6 eV corresponds to F-Ti bonds and the peak at 688.4 eV can be assigned to C-F bonds. The efficiency of the removal/dissolution of CFx and TiFx by the wet chemistries can be clearly demonstrated using this 45 nm test structure. For instance, dilute HF and TMAH:H_2O_2 mixture are efficient for TiFx removal but only show very limited dissolution of CFx polymer. In the presentation, the change in the low-k dielectric and TiN properties due to the plasma etch and subsequent wet cleans will also be presented and discussed.

11:40am **PS-TuM12 Cryogenic Etching of Porous Organosilicate Low-k Materials: Reduction of Plasma Induced Damage**, ***Floriane Leroy***, *T. Tillocher,* GREMI CNRS/Université d'Orléans, France, *L. Zhang,* IMEC, KU Leuven, Belgium, *P. Lefaucheux,* GREMI CNRS/Université d'Orléans, France, *K. Yatsuda,* TEL, Japan, *K. Maekawa,* TEL Technology Center, America, LLC, *J.-F. de Marneffe, M. Baklanov,* IMEC, Belgium, *R. Dussart*, GREMI CNRS/Université d'Orléans, France

Porous Organosilicate (OSG) low-k materials were introduced as inter-metal dielectrics, in order to reduce RC signal delay and energy dissipation. Low-k value is achieved by enlarged open porosity and pore size, but integration of porous low-k is impeded by plasma induced plasma (PID). Several low-damage processes have been reported in the literature. Recently, cryogenic etch, using SF_6-based plasma, was studied as an alternative approach [1]. It was observed that the PID is reduced by decreasing the wafer temperature to cryogenic region (-120°C). At such a low temperature, a passivation layer forms on the pore sidewalls in the low-k bulk, and minimize reaction with damaging radicals.

In this work, we investigate the mechanisms behind this cryogenic low damage process on blanket sample glued on a SiO_2 carrier wafer. The etch rate and the refractive index were measured by in-situ ellipsometry and ex-situ FTIR was used to evaluate methyl group depletion. Species desorbed during the warm-up of the cooled OSG films were detected by a mass spectrometer mounted on the diffusion chamber. In the case of a pure SF_6 plasma, the main desorbed species are C_xF_y, SF_x, SO_xF_y and SiF_x. SOF_2^+ increases first from -120°C to -80°C and decreases from -80°C to 20°C, which shows that a strong desorption of SOF_4 occurs in this range of temperature and play a major role in SF_6 silicon etching [2]. SiF_3^+ and $C_2F_4^+$ mainly desorb at -60°C. It is known that SiF_4 is involved in passivation mechanisms for cryogenic etching, but this result suggests that fluorocarbon species also play a significant role. This is why it was proposed to add C_4F_8 to further protect the low-k material. This new SF_6/C_4F_8 chemistry was studied for various temperatures (from -120°C to +20°C). PID were minimized at -120°C and lower than with pure SF_6. In addition, the increase of the refractive index during the etching process reveals that C_4F_8 condenses into the pores, which is believed to enhance the protection of the material. The desorption of the C_xF_y, SF_x, and SiF_x species is still observed by mass spectrometry. It appears that SiF_3^+ and $C_2F_4^+$ peaks intensity exhibit two local maxima: -120°C, due to desorption of condensed C_4F_8, and -60°C, due to the desorption of the passivation layer. In addition, in-situ XPS experiments was carried out to determine the fluorine based stoichiometry of the passivation layer [3]. Finally, profiles etched with SF_6/C_4F_8 chemistry at -120°C will be presented.

[1] L. Zhang *et al.,* ECS J. Solid State Sci. Technol. 2(6), N131-N139 (2013)

[2] X. Melhaoui *et al.*, J. Appl. Phys 98, 104901 (2005)

[3] J. Pereira *et al.,* Appl. Phys. Lett. 94, 071501 (2009)

12:00pm **PS-TuM13 Remote Shielded Microwave Mini Plasma Source for Sample Cleaning**, ***Herman Bekman***, *R.J. Bolt, F.A. Nennie, P.M. Muilwijk, F.T. Molkenboer, N.B. Koster, O. Kievit*, TNO Technical Sciences, Netherlands

In EUV contamination control, but also more generally, there is a desire for a cleaning technique that can remove hydrocarbon contaminants without inflicting damage to the underlying substrate, e.g. in electron microscopy. Plasma cleaning based on shielded microwave using hydrogen is such a cleaning technique. Generally microwave plasma cleaners are quite big, but at TNO we are pursuing miniaturized plasma cleaners to enable local in-situ cleaning.

In an earlier attempt a mini plasma cleaner has been developed based on a resonant cavity partially filled with a high dielectric material. The source could be operated inside a vacuum system. Due to unexpected thermal issues the source operated only a limited number of times. Furthermore we experienced that it was difficult to judge from the outside why the plasma source was not igniting anymore. A desire for detailed diagnostics during plasma ignition attempts was evident.

A second generation mini microwave plasma cleaner was subsequently designed, built, and tested. The aim was to realize a mini plasma cleaner that should fit on small load locks. Thus substrate could be cleaned prior or after an inspection/processing step. A microwave test setup was designed that allowed simultaneous supply of high power microwave signal at a fixed microwave frequency, for ignition of the plasma, and supply of a low power swept microwave frequency signal for resonator characterization.

This presentation will focus on realization and characterization of the mini plasma source. Cleaning rate as well as detailed microwave characterization measurements have been performed. The microwave measurements demonstrated in real time the effect of plasma ignition on resonance behavior of the cavity.

Advanced Surface Engineering
Room: 212A - Session SE+PS+SM-TuM

Atmospheric Pressure Plasmas, CVD and Other Deposition Methods

Moderator: Hana Barankova, Uppsala University, Sweden, Michael Stueber, Karlsruhe Institute of Technology

8:00am **SE+PS+SM-TuM1 Synthesis of Hybrid Nanoparticles - Fluorinated (Super)Hydrophobic Coatings by Atmospheric Plasma : Possibilities and Challenges**, *J. Mertens, J. Hubert, N. Vandencasteele,* ***François Reniers***, Université Libre de Bruxelles, Belgium

In order to obtain superhydrophobic coatings, one has to combine a low surface energy surface with a specific roughness. We propose a simple method to obtain such coatings by depositing by atmospheric plasma fluorinated coatings starting from C_6F_{12} or C_6F_{14} in argon or helium onto surfaces previously decorated with SiO_2 or TiO_2 nanoparticles. The loading (concentration) and size of nanoparticles were varied, as well as the plasma parameters (nature of the process gas and precursor, plasma power, deposition time). Depending on the experimental parameters, coatings exhibiting water contact angles from 110° to more than 160° could be obtained. The mechanisms for the polymer synthesis have been studied by a combination of atmospheric mass spectrometry and X-ray photoelectron spectroscopy, and the influence of the process gas on the final chemical structure of the coating is evidenced and explained. A higher fragmentation pattern is shown for Argon, due to the higher electron density and the higher energy available in the filamentary discharge. This is responsible for a change in the CF_2 and CF_3 moieties in the final coating. Similarly, the nature of the oxide nanoparticles has a strong influence on the chemistry of the coating: whereas SiO_2 particles do not modify the CFx films, the TiO_2 nanoparticles contribute to a significant degradation of the chemistry of the coating. This method can easily be implemented on any industrial process line, provided a good adhesion of the final coating on the subtrate is obtained.

8:20am **SE+PS+SM-TuM2 Deposition of Antifouling PMOXA-like Coatings using Atmospheric Pressure Helium Plasma Jet**, ***Sameer Al-Bataineh***, *A. Cavallaro, M. Ramiasa, K. Vasilev*, University of South Australia

Antifouling interfaces are important in a wide range of applications such as food packaging, water purification, marine biofouling and biomedical devices.[1,2] In recent years, poly(2-oxazoline)s have attracted much attention due to their numerous biological applications as antifouling polymers.[3,4] Poly(2-methyl-2-oxazoline)(PMOXA) has antifouling properties comparable to the gold standard PEG, and has better stability in a range of aqueous solution and biological media.[5] Atmospheric pressure plasma (APP) is an emerging technology with a wide range of applications including material processing.[6] The advantage of using APP for surface modification is that it eliminates the use of expensive vacuum equipment and enables continuous surface modification processes. This study aims to develop PMOXA-like coatings using atmospheric pressure helium plasma jet.

The plasma jet system used in this study consisted of a glass capillary tube with an internal diameter of 1mm that was surrounded by two external hollow electrodes separated by 4mm. The carrier helium gas was sent through a glass container at a flow rate of $1L.min^{-1}$ and carried the oxazoline monomer (2-methyl-2-oxazoline, MOXA) vapour into the glass tube. The plasma jet was operated at an applied voltage of 5.5 kV_{pk-pk} and a frequency of 10 kHz. Deposition of the plasma coatings was carried out under static deposition conditions with 3mm separation distance between the end of the capillary tube and the substrate. To enhance stability of the coatings, substrates were heated during plasma deposition process.

Surface elemental composition and molecular structure of oxazoline plasma polymer coatings were thoroughly characterised using XPS and ToF-SIMS. Stability of the plasma coatings were examined by incubation in PBS buffer solution at room temperature overnight. The antifouling properties of the plasma coatings are now under investigation towards resisting protein adsorption and bacterial cell adhesion. In addition, the surface chemistry and functionality of the coatings produced in this study will be briefly compared to those prepared with an RF low pressure plasma.[7]

This study offers a convenient alternative single step strategy for preparation of oxazoline-based antifouling coatings.

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2. Zou L, et al., *J. Membr. Sci.*, 2011, 369, 420.

3. Luxenhofer R, et al., *Macromol. Rapid Commun.,* 2012, 33, 1613.

4. Sedlacek O, et al., *Macromol. Rapid Commun.,* 2012, 33, 1648.

5. Konradi R, et al., Langmuir, 2008, 24, 613.

6. Merche D, et al., *Thin Solid Films*, 2012, 520, 4219.

7. Ramiasa MN, et al., *Chem. Commun.,* 2015, 51, 4279.

8:40am **SE+PS+SM-TuM3 Antibacterial Silicon Oxide Thin Films Doped with Zinc and Copper Grown by Atmospheric Pressure Plasma Chemical Vapor Deposition**, *E. Jäger,* Montanuniversität Leoben*, J. Schmidt, A. Pfuch, S. Spange, O. Beier,* INNOVENT e.V.*, O. Jantschner, R. Daniel,* Montanuniversität Leoben*,* ***Christian Mitterer***, Montanuniversität Leoben, Austria

Zn- and Cu-doped SiO_x films were applied by atmospheric pressure plasma chemical vapor deposition to study their antibacterial efficiency against Gram-negative *Escherichia coli* and their cytotoxic effect on the growth of mouse cells. ZnO_x and CuO_x particles were found to be homogeneously embedded within the SiO_x films. For both doping elements, bacteria are killed already within the first three hours after exposure to the film surface. In contrast, mouse cells grow well on the surfaces of both film types, with a slight inhibition effect present only after the first day of exposure, due to the more pronounced release of zinc and copper. The obtained results indicate that the films show a high potential for use as effective antibacterial surfaces for medical applications

9:00am **SE+PS+SM-TuM4 Carbon Bridge Incorporation in Organic-Inorganic Hybrid Coatings using Atmospheric Plasma Deposition in Ambient Air**, ***Linying Cui***, Stanford University*, G. Dubois,* IBM Almaden Research Center*, R.H. Dauskardt*, Stanford University

Atmospheric plasma deposition in ambient air has a huge potential for large-scale coating synthesis at reduced cost for energy, display, and aerospace applications. However, the abundant oxygen in air poses significant oxidation challenge for incorporating specific oxygen sensitive components in the coating. In this work, the oxygen sensitive carbon bridge structure was successfully incorporated into the inorganic silicate network in the oxygen-helium atmospheric plasma in ambient air. The mechanism of incorporating the specific carbon structure in an oxidative species rich environment was elucidated by a kinetics model which takes into account the probability of oxidation, adsorption, and desorption of different precursor species during gas transport and on the substrate surface. The key tuning knobs were identified as the precursor chemistry and the precursor delivery rate. The resulting carbon bridged organo-silicate coatings exhibited significantly improved plasticity, more than doubled adhesion, and up to four times increase of moisture resistance in terms of the driving energy threshold for debonding in humid air, compared to plasma silica coatings and commercial sol-gel polysiloxane coatings. In order to further improve the interfacial bonding of the coating to oxygen sensitive substrate in an oxidative atmospheric plasma environment, other deposition parameters were also investigated in order to fully activate but not over-oxidize the substrate. The resulting carbon bridged, highly adhesive coating showed remarkably enhanced hydrothermal stability, a key requirement for application in exterior coatings and functional membranes. As an example for application, the carbon-bridged coating was deposited between hard scratch-resistant coatings and oxygen-sensitive polymer substrate to enhance the adhesion of hard coatings for airplane window protection.

9:20am **SE+PS+SM-TuM5 Atmospheric Plasma in Liquids**, ***Ladislav Bardos***, *H. Barankova*, Uppsala University, Sweden **INVITED**

Experiments using spark discharge above the water level were reported already in 1784 by Henry Cavendish after his study of air. His results inspired in 1894 Lord Rayleigh and William Ramsay and led to an important discovery of argon present in air. Studies of water electrolysis and interactions of a glow discharge with water solutions were described in 1887 by J. Gubkin and followed in 1952 by R.A. Davies and A. Hickling. The first type of plasma discharge submerged directly into water was an arc. The arc discharges are used for the underwater welding already since 1930.

A number of applications of submerged arcs have already been tested and reported. Rapid developments of non-thermal (cold) atmospheric plasma sources during last century led to new studies of plasma in liquids. Studies of the plasma-assisted electrolysis and different phenomena observed on surfaces of electrodes during electrolysis in water electrolytes enhanced an interest in different types of submerged discharges. New processes were developed like the plasma electrolytic oxidation (PEO), formation of nanoparticles and nanotubes, novel plasma-chemical reactions, plasma cleaning, disinfection and "activation" of water or water solutions. This presentation summarizes several interesting systems and results on the submerged plasma in liquids. Examples of the experimental systems and the results of tests of cold plasma discharges in water using different power generators and an efficient low power production of hydrogen from the mixtures of water with ethanol will be presented and discussed in more details.

11:00am **SE+PS+SM-TuM10 Study of Polymer Confinement Effects in Nanocomposite Thin Films Synthesized by Initiated Chemical Deposition**, ***Chia-Yun(Sharon) Hsieh***, *K.K.S. Lau*, Drexel University

Initiated chemical vapor deposition (iCVD) is a liquid-free polymer synthesis technique that simultaneously deposits the polymers as thin films on supporting substrates. It produces well-defined polymers that are spectroscopically identical to corresponding polymers synthesized in the liquid phase. A wide range of polymers have been produced by iCVD, including hydrophilic polyglycidol (PGL), hydrophobic polytetrafluoroethylene (PTFE), semicrystalline polyethylene oxide (PEO), and amorphous poly (methyl methacrylate) (PMMA). In addition, iCVD is an effective approach for integrating polymers within porous 3D inorganic nanostructures to produce polymer nanocomposite thin films. By utilizing inorganic nanostructural templates such as mesoporous TiO_2 nanoparticle networks, good dispersion of the nanoparticles can be ensured by adopting well-established dispersion procedures. Conformal and uniform polymer growth within the pore space can be achieved by operating under reaction-limited iCVD conditions that allow efficient delivery of reactive precursors by gas and surface diffusion. Quantitative measurements using thermogravimetric analysis has shown that 90–100% of the available pore space can be filled in porous layers of up to 12 μm in thickness with 10–20 nm diameter interconnected pores. As a result, we are able to achieve polymer nanocomposite thin films with high inorganic content (>80 wt%) that are well-dispersed. This ability provides an ideal platform for studying polymer confinement effects that lead to significantly altered polymer properties compared to its bulk 2D planar film counterpart with no inorganic filler. For example, iCVD PGL-TiO_2 nanocomposite thin films has shown a significant increase of 50–60°C in the polymer glass transition temperature (a transition between the glassy, brittle state to the rubbery, pliable state) compared with bulk PGL. This has been attributed to the strong hydrogen bonding interactions between the polar oxygen groups on PGL with the hydroxyl groups on the TiO_2 surface. Here, we will detail the iCVD approach in making different polymer nanocomposite thin films and discuss the resulting nanoscale confinement effects on polymer properties as a result of different polymer-substrate interactions. This knowledge has critical implications in applying polymers in the design of nanostructured devices as bulk polymer properties might not be followed in these systems.

11:20am **SE+PS+SM-TuM11 Persistent Superhydrophilicity of Polycarbonate Surfaces *via* Nanoimprint Lithography *and* Atomic Layer Deposition**, ***Xue Li***, Institute of Materials Research and Engineering (IMRE), Singapore*, K.S.L. Chong, M.S.M. Saifullah, R.B. Yang, C.S. Lee, Y.C. Loke,* Institute of Materials Research and Engineering (IMRE)*, A.Y. He*, Loke

Superhydrophilic surfaces are often exploited for their anti-fog ability and typically rely on coatings which modify the surface energies of the materials to create such effects. Such traditional coatings are often applied wet and are not long lasting. A persistent superhydrophilic coating with both anti-fog and anti-UV properties have been fabricated on polycarbonate (PC) surfaces *via* a combination of nanoimprint lithography and atomic layer deposition (ALD) process. Nanoimprint lithography was used to pattern anti-reflection (AR) structures on to a PC surface. These samples were then coated with a thin layer titanium dioxide (TiO_2) layer *via* a low temperature ALD process (<80 °C). The PC sample with AR patterns demonstrated enhanced visible light transmittance upto 94% and reduced transmittance in the UV wavelengths (<400 nm). The TiO_2 layer is superhydrophilic and the resultant samples showed a persistent superior anti-fog effect. More importantly, the superhydrophilicity can be recycled via rinsing in an oxidant solution, and had demonstrated stability upto 4 months.

11:40am **SE+PS+SM-TuM12 Enhanced CO_2 Permeation Characteristics Performance On A Crack-Free Nanostructured Ceramic Membrane**, ***Ngozi Nwogu***, *E. Gobina*, Robert Gordon University, UK

Carbon capture from point source emissions have been acknowledged as one of numerous strategies required for alleviating unrestricted release of greenhouse gases (GHGs) into the atmosphere. To keep greenhouse gases at controllable levels, large drops in CO_2 emissions through capturing and separation will be necessary. Reduction and manipulation of materials at nanometre scale are key experiments in nano-science and nanotechnology. In this work, an experimental study is made on the preparation, the morphological characterization and the gas permeation of ordered ceramic multilayer membranes with silica top layer. We developed and manufactured a crack-free thin film membrane on a fresh tubular alumina ceramic membrane with pore diameter of 6000nm. By using a hybrid material of appropriate proportion, the nano-fabrication conditions are then controlled with extremely high carbon dioxide permeance due to the membrane immersion in a silica solution. Results obtained from the experiments show that the nanostructured silica membranes have potential applications in the treatment of large gas streams under low pressure conditions like carbon dioxide separation from flue gases.

Keywords: Carbon capture, CO_2 Permeation, nanostructured ceramic membrane & flue gases

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]

1. D. B. Ingram, S. Linic, JACS, 133, 5202, 2011

2. Suljo Linic, Phillip Christopher and David B., Nature Materials, 10, 911, 2011.

3. Ingram P. Christopher, H. Xin, S. Linic, Nature Chemistry, 3, 467, 2011.

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5. M. Andiappan, J. Zhang, S. Linic, Science, 339, 1590, 2013

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.

ACKNOWLEDGEMENTS

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

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.

Surface Science
Room: 113 - Session SS+AS+EN-TuM

Mechanistic Insight of Surface Reactions: Catalysis, ALD, etc. - I
Moderator: Ludwig Bartels, University of California - Riverside

8:00am **SS+AS+EN-TuM1 Active Sites of Nitrogen-Doped Carbon Materials for Oxygen Reduction Reaction**, ***Takahiro Kondo****, D. Guo, R. Shibuya, C. Akiba, S. Saji, J. Nakamura*, University of Tsukuba, Japan

Nitrogen-doped carbon materials have been found to demonstrate high electrocatalytic activity for oxygen reduction reaction (ORR) as the non-metal catalysts but the active site is still under debate. This is due to the complexity of the real catalysts, such as mixing of different type of N and inhomogeneity in both structure and conductance. Here we designed the nitrogen doped graphite (HOPG) model catalysts with different type of N dominance and its concentration to directly clarify the ORR active site. ORR measurements showed that active site was created by pyridinic N (N bonded to two carbon atoms). The ORR active site was ascribed to the carbon atom with Lewis base property created by neighbour pyridinic N based on the investigations of intermediate state of ORR, localized electronic states at carbon next to pyridinic N and CO_2 adsorption property by X-ray photoelectron spectroscopy (XPS), scanning tunneling spectroscopy (STS) and temperature programmed desorption (TPD), respectively. The ORR activity of model catalyst per pyridinic N concentration was then found to be in good agreement with that for real nitrogen-doped graphene catalyst.

8:20am **SS+AS+EN-TuM2 Cerium Oxide-Induced Intercalation of Oxygen on Supported Graphene**, ***Zbynek Novotny****,* Pacific Northwest National Laboratory*, F.P. Netzer,* Karl-Franzens University, Austria*, Z. Dohnalek*, Pacific Northwest National Laboratory

Cerium oxide is an important catalytic material known for its ability to store and release oxygen, and as such, it has been used in a range of applications, both as an active catalyst and as a catalyst support. Using scanning tunneling microscopy and Auger electron spectroscopy, we investigated oxygen interactions with CeO_x clusters on a complete graphene monolayer-covered Ru(0001) at elevated temperatures (550 – 700 K). Under oxidizing conditions ($\sim10^{-7}$ Torr of O_2), oxygen intercalation under the graphene layer is observed. Time dependent studies demonstrate that the intercalation starts in the vicinity of the CeO_x clusters and extends until a completely intercalated layer is observed. Atomically resolved images further show that oxygen forms p(2×1) structure underneath the graphene monolayer. Temperature dependent studies yield an apparent kinetic barrier for the intercalation of 0.9 eV. This value correlates well with the theoretically determined value for the reduction of small CeO_2 clusters reported previously. At higher temperatures, the intercalation is followed by a slower etching of the intercalated graphene (apparent barrier of 1.1 eV). The intercalated oxygen can also be released through the CeO_x clusters by annealing in vacuum. In agreement with previous studies, no intercalation is observed on a complete graphene monolayer without CeO_x clusters, even in the presence of a large number of point defects. These studies demonstrate that the easily reducible CeO_x clusters act as intercalation gateways capable of efficiently delivering oxygen underneath the graphene layer.

8:40am **SS+AS+EN-TuM3 Dissociation Dynamics of Energetic Water Molecules on TiO_2(110): Combined Molecular Beam Scattering and Scanning Tunneling Microscopy Study**, *Z.-T. Wang, Y.-G. Wang, R.T. Mu, Y. Yoon, G.A. Schenter, R. Rousseau, I. Lyubinetsky, **Zdenek Dohnalek***, Pacific Northwest National Laboratory

Molecular beam scattering techniques have proven extremely useful in determining the dynamics of energy flow in the course of chemical reactions. We have successfully designed and constructed a unique, state of the art instrument combining a molecular beam scattering source coupled with a low temperature scanning tunneling microscope (STM). The combination of these techniques allows us to follow the same area during adsorption and image surface species as a function of incident energy of reacting molecules. Our first study focuses on reversible water dissociation on Ti rows of TiO_2(110), which leads to the formation of pairs of terminal and bridging hydroxyl species, $H_2O \leftrightarrow HO_t + HO_b$. The results of our measurements show the onset of H_2O dissociation at 0.2-0.3 eV of incident energy, independent of whether the molecules impinge along or across the Ti rows at an incident angle of 60° relative to surface normal. Following the onset, the dissociation probability increases linearly with increasing incident energy. Ensembles of *ab initio* molecular dynamics (AIMD) simulations at several incident energies reproduce the product distribution seen in the STM. Additionally, these studies show that the dissociation occurs only for the impacts in the vicinity of surface Ti ions with an activation energy of 0.3 eV and that the O-H bond cleavage is accomplished within the time of a single vibration. The AIMD simulations were further used to construct a classical potential energy surface for water/TiO_2(110) interactions and execute non-equilibrium classical MD simulations that closely reproduce the onset and linear energy dependence of the dissociation probabilities.

9:00am **SS+AS+EN-TuM4 Tracking Site-Specific C-C Coupling of Formaldehyde Molecules on Rutile TiO_2(110)**, ***Zhenrong Zhang****, K. Zhu, Y. Xia,* Baylor University*, M. Tang,* Southern Illinois University Carbondale*, Z.-T. Wang, I. Lyubinetsky,* Pacific Northwest National Laboratory*, Q. Ge,* Southern Illinois University Carbondale*, Z. Dohnálek,* Pacific Northwest National Laboratory*, K. Park*, Baylor University

We report the direct visualization of molecular coupling of the smallest aldehyde, formaldehyde, on reduced rutile TiO_2(110) surfaces using scanning tunneling microscope (STM). Images from the same area at viable temperatures (75 ~ 170 K) show that formaldehyde preferably adsorbs to bridging-bonded oxygen vacancy (V_O) defect site. V_O-bound formaldehyde couples with Ti-bound CH_2O form a diolate species, which stays stable at room temperature. In addition, two V_O-bound formaldehyde molecules can couple and form Ti-bound species, which desorbs above ~215 K. This coupling reaction heals both the V_O sites indicating formation and desorption of ethylene. We also directly observed the diffusion of methylene groups to nearby empty V_O sites formed upon dissociation of the C-O bond in V_O-bound formaldehyde, which suggests that the ethylene formation is via coupling of the methylene groups.

9:20am **SS+AS+EN-TuM5 AVS 2014 Gaede-Langmuir Invited Talk: Models for Heterogeneous Catalysts: Complex Materials at the Atomic Level**, ***Hajo Freund*****, Fritz Haber Institute of the Max Planck Society, Germany **INVITED**

Our understanding of catalysis, and in particular heterogeneous catalysis, is to a large extend based on the investigation of model systems. The enormous success of metal single crystal model surface chemistry, pioneered by physical chemists, is an outstanding example. Increasing the complexity of the models towards supported nanoparticles, resembling a real disperse metal catalyst, allows one to catch in the model some of the important aspects that cannot be covered by single crystals alone. One of the more important aspects is the support particle interface. We have developed strategies to prepare such model systems based on single crystalline oxide films, which are used as supports for metal, and oxide nanoparticles, which may be studied at the atomic level using the tools developed in surface science. However, those oxide films may also serve as

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*** Gaede Langmuir Award Winner**

reaction partners themselves, as they are models for SMSI states of metal catalyst. Using such model systems, we are able to study a number of fundamental questions of potential interest, such as reactivity as a function of particle size and structure, influence of support modification, as well as of the environment, i.e. ultra-vacuum or ambient conditions, onto reactivity. The thin oxide film approach allows us to prepare and study amorphous silica as well as 2D-zeolites. Those systems, in spite of their complexity, do lend themselves to theoretical modelling as has been demonstrated.

11:00am **SS+AS+EN-TuM10 The Solid State Li-CoO Conversion Reaction Studied by ARXPS and STM**, ***Ryan Thorpe***, *S. Rangan,* Rutgers, the State University of New Jersey*, A. Howansky,* Stony Brook University*, R.A. Bartynski*, Rutgers, the State University of New Jersey

Cobalt (II) oxide is a promising electrode material for Li-ion conversion batteries, undergoing the following reversible redox reaction upon exposure to lithium:

$2Li + CoO \leftrightarrow Li_2O + Co^0$.

In order to characterize the phase progression and morphology of the Li-CoO reaction, epitaxial CoO(100) and (111) films were exposed to lithium in an ultra-high vacuum chamber. The early stages of the reaction were then characterized with scanning tunneling microscopy (STM), while the diffusion of Li into the films and resultant reduction of CoO was quantified using angle-resolved x-ray photoemission spectroscopy (ARXPS). From these measurements, a model of the Li-CoO reaction was constructed for each orientation.

For CoO(111) films, the conversion reaction initiated at step edges and defect sites before proceeding across the surface of the film. STM images of CoO(111) after 0.2 ML of Li exposure suggest that the conversion reaction products initially assumed a periodic structure which was in registry with the CoO(111) surface. For larger Li exposures, ARXPS measurements indicated that the reaction proceeded in a layer-by-layer fashion into the bulk, maintaining a planar interface between reacted and unreacted CoO.

The reaction of the CoO(100) surface with 0.1 ML of Li resulted in the formation of 2-3 nm Co metal nanoparticles which decorated the CoO step edges. Upon further lithiation, the conversion reaction proceeded into the film preferentially at step edges. ARXPS measurements suggested that the reaction penetrated deep into the CoO film from these nucleation points before spreading across the rest of the surface. These combined results show the importance of crystallographic orientation in determining the reaction kinetics in a Li-ion battery.

11:20am **SS+AS+EN-TuM11 Imaging Water Adsorption and Dissociation on RuO_2 (110) Surfaces**, ***Rentao Mu***, *D.C. Cantu, X. Lin, V.A. Glezakou, Z.-T. Wang, I. Lyubinetsky, R. Rousseau, Z. Dohnálek*, Pacific Northwest National Laboratory

Understanding water/solid interactions is a current critical scientific challenge with important implications for a variety of fundamental and applied processes. Here we study the interactions of water with RuO_2, which has a wide range of applications in photocatalytic water splitting, heterogeneous catalysis, electrochemistry and many other energy-related areas. We prepared stoichiometric (*s*-), reduced (*r*-) and oxidized (*o*-) $RuO_2(110)$ surfaces and studied water adsorption, dissociation, and diffusion using time-lapsed scanning tunneling microscopy and density functional theory calculations. On *s*-$RuO_2(110)$ we show that water monomers become mobile above 238 K and form dimers which are immobile below 273 K. More importantly, we find that the mobile water dimers dissociate readily to form Ru-bound H_3O_2 and hydroxyl species (HO_b) on bridging oxygen (O_b) rows. The onset for diffusion of H_3O_2 on *s*-$RuO_2(110)$ is observed at ~273 K, indicating a significantly higher diffusion barrier than that for water monomers. The experimentally determined diffusion barriers are in agreement with those obtained from the DFT calculations. The observed behavior is compared and contrasted with that observed for water on isostructural rutile $TiO_2(110)$ where both molecularly-bound monomers and dimers are in equilibrium with their deprotonated states. In contrast with $TiO_2(110)$, the larger separation of Ru atoms induces the segmentation of water chains at high water coverages. On slightly oxidized *o*-$RuO_2(110)$, water molecules react with oxygen adatoms (O_a's) on Ru rows and form pairs of terminal hydroxyl groups which can reversibly dissociate back to a water molecule and O_a. This process results in the displacement of O_a's along the Ru rows. Along- and across-row diffusion of isolated water molecules is tracked at room temperature on both slightly, and heavily oxidized *o*-$RuO_2(110)$ by following the position of hydroxyl pairs. On *r*-$RuO_2(110)$, we find that water molecules readily dissociate at bridging oxygen vacancies and form bridging hydroxyl groups. The mechanism of along- and across-row diffusion of the bridging hydroxyl protons is also studied at room temperature. The atomically-detailed, quantitative assessment of binding and diffusion of the surface species formed upon water adsorption on $RuO_2(110)$ represent a critical step in achieving fundamental level understanding of the role RuO_2 plays as H_2 and O_2 evolution co-catalysts in photocatalytic water splitting reactions.

11:40am **SS+AS+EN-TuM12 Surface Reaction Kinetics during Low Temperature ALD of Al_2O_3 Studied by Broadband Sum-frequency Generation**, ***Vincent Vandalon***, *W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

The nonlinear optical technique of broadband sum-frequency generation (BB-SFG) has been used to study the surface reactions during atomic layer deposition (ALD). Vibrational BB-SFG spectroscopy is excellently suited for *in-situ* studies of the surface chemistry governing ALD because of its inherent interface selectivity, submonolayer sensitivity, and short acquisition times. In contrast to BB-SFG, conventional absorption spectroscopy, based on the so called "differential" measurements, monitors only changes on the surface. On the other hand, due to its surface selectivity, BB-SFG reveals information about both *persistent* and *changing* surface groups. Therefore, with this technique, open questions can be addressed such as the origin of the decrease in growth per cycle (GPC) at low temperatures of the ubiquitous process of thermal ALD of Al_2O_3 from $Al(CH_3)_3$ and H_2O. So far, a complete picture of the surface chemistry explaining the reduced GPC is missing and the exact cause of the limited growth at low temperatures remains unclear.

More particularly, the surface chemistry of thermal ALD Al_2O_3 was followed by monitoring the density of the $-CH_3$ surface groups. In contrast to ALD at high temperatures, below 200^oC it was observed that a significant amount of $-CH_3$ could not be removed during the water half-cycle. The observed kinetics could not be explained by a thermally-activated first-order reaction with a constant cross section. We investigated the temperature dependence of the reaction kinetics further by measuring the $-CH_3$ coverage as a function of precursor and co-reactant exposure at different temperatures. It found that the absolute cross section obtained for the TMA half-cycle was independent of temperature, indicating that the chemisorption of TMA is not a thermally activated process. The behavior during the water half-cycle was found to be more complex showing a strong dependence on temperature; it cannot be described as a reaction simply obeying Arrhenius behavior. This is in line with the more complex behavior predicted by recent DFT work carried out by Shirazi and Elliott [Nanoscale 2015] where a so-called "cooperative" effect was observed leading to a coverage dependent reactivity. The observations presented in this work are direct experimental evidence of such a "cooperative" effect and were only possible due to the inherent surface selectivity of BB-SFG.

12:00pm **SS+AS+EN-TuM13 The Preparation and Redox Properties of $Cu/Al_2O_3/ZnO(0001)$ Model Surfaces**, *J. Hu, J.J. Huang, H. Zhang,* ***Mingshu Chen***, Xiamen University, China

The $Cu/Al_2O_3/ZnO(0001)$-Zn ternary model catalysts were prepared and characterized by XPS and LEISS. The Al_2O_3/ZnO was prepared by depositing Al onto the ZnO surface in O_2 atmosphere at 523 K, and Cu/ZnO was prepared by depositing Cu onto ZnO surface at room temperature. It was found that Al_2O_3 grew on the ZnO surface by a layer-by-layer model, while Cu formed two-dimensional islands only at low coverage and three dimensional clusters at high coverage. For $Cu/Al_2O_3/ZnO(0001)$-Zn, the XPS and LEIS spectra showed that the copper islands were preferred on the interfaces of Al_2O_3/ZnO. Comparing to the Cu/ZnO binary model catalyst, the addition of Al_2O_3 obviously slowed down the reduction of $Cu/Al_2O_3/ZnO$ by H_2. More significantly, the existence of Al_2O_3 in the ternary model catalyst leaded to an increase of Cu^+ concentration. The enhancement of Al_2O_3 in $Cu/Al_2O_3/ZnO(0001)$-Zn for methanol synthesis may origin from that the Al_2O_3 helps to stabilize the surface Cu^+ which has been proposed as one of the active sites.

Thin Film
Room: 111 - Session TF+EM+MI+MS-TuM

ALD for Alternative Devices
Moderator: Paul Poodt, Solliance/TNO, Richard Vanfleet, Brigham Young University

8:00am **TF+EM+MI+MS-TuM1 FAST-ALD^{TM} with Close Proximity (CP) Plasma for Low Temperature Applications: Nano-Composite Layer (NCL) Stacks for Flexible Substrates**, ***SangIn Lee***, Veeco **INVITED**

The stress of the film is an important factor in mechanical stability and reliability of the devices, especially flexible electronic applications and microelectro-mechanical systems (MEMS), because it causes mechanical cracks, delamination and degradation in reliability of the device. Moreover, mechanical integrity of nano-scaled devices requires not only the physical properties of the individual films such as thermal expansion coefficient and elastic modulus, but also integral structural properties such as interface adhesion, and therefore residual stress of the film need to be managed.

Veeco's proprietary ALD technology, Fast Array Scanning Technology (FAST-ALD™) with Close-Proximity (CP) Plasma, has unique characteristics that are differentiated from other spatial ALD technologies. CP-plasma in FAST-ALD™ provides very uniform radical streams onto the substrate without plasma-induced damages and substrate heating enabling FAST-ALD™ to provide plasma-ALD films and stable polymeric MLD films from CP Plasma which cannot be obtained from conventional plasma process, for high-quality films at extremely low temperature for use in stress-sensitive device applications such as low-k films on Si wafers or flexible functional films on plastic substrates.

Stresses in inorganic ALD layers can be offset by either carbon-incorporated dielectric (CID) interlayers or polymeric MLD interlayers. The relative percentage of the inorganic ALD film to CID interlayer can be changed to tailor the stress of the stacked film to the device requirements. In this experiment, the combinations of an inorganic dielectric layer (Al_2O_3) with CID interlayers as part of nano-laminates, obviously in the same philosophy with polymeric MLD interlayers, nano-composite layer (NCL) stacks were deposited at 80°C to control the stress of the stacks from tensile to compressive state and vice versa, by changing the thickness and atomic content of Al_2O_3 layer and materials. By changing the ratio of the thickness in NCL stacks, 4:2 stacked film (4 Al_2O_3 layers and 2 CID layers as a sub-stack) and 1:1 stacked film (1 Al_2O_3 layer and 1 CID layer as a sub-stack) with total 30nm thickness show very low tensile stress and compressive stress of +58MPa and -89MPa, respectively, indicating the potential application of these free standing film stacks to nano-scaled devices and/or environmentally sensitive devices. NCL stack shows higher immunity to cracks and competitive barrier properties than that of the single ALD layer. NCL concept approaches can be applied to semiconductor in low-k pore sealing and oxidation barrier in the backend-of-line (BEOL) and cutting-edge devices with flexible substrates.

8:40am **TF+EM+MI+MS-TuM3 Atmospheric Roll-to-Roll Spatial Molecular Layer Deposition for flexible barriers**, ***Fieke van den Bruele***, *F. Grob, P. Poodt*, Holst Centre / TNO, Netherlands

Proper encapsulation of devices such as OLEDs and thin-film photovoltaics is critical, as exposure to moisture from the ambient will degrade these devices, reducing their efficiency, lifetime, or even lead to failure altogether. Especially for OLEDs, the barrier requirements are very challenging, with a Water Vapor Transmission Rate < 10^{-6} g/m^2/day. To achieve these very low WVRTs, very high quality barrier layers are required, being pinhole free over the entire device area. Encapsulation of flexible devices is even more challenging as the encapsulation should not affect the device flexibility too much.

The recent development of roll-to-roll and large-area Spatial ALD technology has spurred the interest in ALD for encapsulation and barriers. Thin layers of inorganic material (10-20 nm) made with (spatial) ALD have sufficiently low intrinsic WVTR but often do not meet the requirements for barriers because they are very sensitive to particles and roughness that lead to defects. Thick inorganic films are less sensitive to particles, but suffer from stress and can have a limited flexibility. Various flexible thin film encapsulation techniques have been recently developed, often combining one or more thin inorganic diffusion barrier layers (e.g. SiN_x, Al_2O_3) with an organic layer that acts as stress relief layer but has no additional barrier functionality. One of those proposed interlayers for stress relief and flexibility are organic materials deposited through Molecular Layer Deposition (MLD). A well-studied example are the Alucones, prepared by reacting trimethyl aluminum with an alcohol. There are several reports on the barrier properties of Al_2O_3 – Alucone multilayer stacks, but the results seem to be inconclusive.

Assessing the flexibility these MLD layers are is not straightforward as measuring the mechanical properties of these very thin layers is difficult. We use a simple, qualitative method to test the flexibility of these MLD layers, by combining bending test with a polymer etch test to visualize cracks and other defects in the MLD film caused by bending. Preliminary results show that the flexibility of MLD layers, like their organic counterparts, largely depend on film thickness and can suffer from instability.

The next step in making MLD barriers is upscaling towards large-area and roll-to-roll production. We will present the results of our atmospheric roll-to-roll spatial MLD of alucones on polymer foils. Furthermore, an outlook to full-industrial scale R2R ALD/MLD production of barriers will be discussed.

9:00am **TF+EM+MI+MS-TuM4 Low Temperature, Temporal and Spatial Atomic Layer Deposition of TiO_2 using Titanium Tetra-Isopropoxide as Precursor**, ***Morteza Aghaee***, Eindhoven University of Technology, Netherlands, *P.S. Maydannik,* Lappeenranta University of Technology, Finland, *P. Johansson,* Tampere University of Technology, Finland, *M. Creatore,* Eindhoven University of Technology, Netherlands, *T. Homola, D.C. Cameron,* Masaryk University, Czech Republic, *J. Kuusipalo*, Tampere University of Technology, Finland

Spatial atomic layer deposition (S-ALD) is a technique which has been shown to lead to high quality moisture barrier films (e.g. Al_2O_3) in a roll-to-roll process[1]. However, TiO_2 is expected to outperform Al_2O_3 because of its higher stability against long-term degradation than Al_2O_3. For high throughput S-ALD at low temperature, highly reactive precursors with high vapour pressure are necessary. Titanium chloride is typically used but has the disadvantages of residual chlorine incorporation in the film and generation of corrosive by-products. Titanium tetra-isopropoxide (TTIP) is a valid alternative because of its high vapour pressure at room temperature compared to other titanium organometallic compounds[2]. TTIP has not previously been used as a precursor for S-ALD.

In this work, a preliminary investigation has been carried out on the temporal ALD approach consisting of alternating exposure of a polyethylene naphthalate (PEN) substrate to the precursors TTIP and water, ozone or oxygen-fed plasma. The deposition was carried out at a substrate temperature of 80-120ºC. The highest growth rate (0.056 nm/cycle) and refractive index (2.33) values have been obtained by using an O_2- fed plasma. The water vapour transmission rates have been found to be lower than 5×10^{-4} g.m^{-2}.day^{-1} at 38°C, 90% RH conditions for a film thickness of 20 nm. For the water process, WVTR values were found to be in the range of 10^{-3} for a 40 nm film.

Based on these results, a low pressure S-ALD process was developed using a Beneq TFS200R system. Titanium dioxide films were successfully deposited by TTIP and water as S-ALD precursors in the same temperature range as temporal, and their properties were characterised in terms of growth per cycle, refractive index and chemical composition. The growth rate saturated at precursor exposure time of 230 ms at every deposition temperature, which was slightly higher than the growth rate in temporal ALD mode at the same temperature range. Similar properties (refractive index and chemical composition) to temporal ALD have been obtained by adopting S-ALD.

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[1] P. S. Maydannik, T. O. Kääriäinen, K. Lahtinen, D. C. Cameron, M. Soderlund, P. Soininen, P. Johansson, J. Kuusipalo, L. Moro, and X. Zeng, J. Vac. Sci. Technol. A **32**, 051603 (2014).

[2] M. Aghaee, P. S. Maydannik, P. Johansson, J. Kuusipalo, T. Homola, M. Creatore, D. C. Cameron, Submitted to J. Vac. Sci. Technol. (2015)

9:20am **TF+EM+MI+MS-TuM5 Spatial Atomic Layer Deposition into Flexible Porous Substrates**, ***Kashish Sharma***, University of Colorado at Boulder, *D. Routkevitic, N. Varaksa,* In Redox, *S.M. George*, University of Colorado at Boulder

Spatial atomic layer deposition (S-ALD) is important for ALD commercialization. S-ALD has been successfully demonstrated on flat substrates. In this work, S-ALD was examined on flexible porous substrates using anodic aluminum oxide (AAO) membranes and Li ion battery electrodes. The AAO membranes were coated with ZnO ALD using diethylzinc and ozone as the reactants. The Li ion battery electrodes were coated with Al O ALD using trimethylaluminum and ozone as the reactants. These experiments utilized a rotating cylinder reactor for S-ALD that is scalable to roll-to-roll operation [K. Sharma et al., , 01A132 (2015)].

ZnO S-ALD into the pores of AAO membranes depends on gas transport that is determined by the pore diameter, pore aspect ratio and reactant pulse duration. The reactant pulse duration is defined by the substrate speed in S-ALD. Different reaction conditions and AAO membrane characteristics were explored using energy dispersive spectroscopy (EDS) to measure the Zn coverage profiles. Substrate speeds were defined by rotating cylinder rates of 10, 100 and 200 revolutions per minute (RPM). The AAO pore diameters were 50, 100 and 150 nm.

For AAO pore lengths of 10 microns, the EDS analysis revealed that uniform Zn coverage profiles were obtained at 10 RPM. The Zn coverage profiles were less uniform at higher RPM values and smaller pore diameters. These results indicate that S-ALD into porous substrates is feasible. However, the uniformity of the ALD coverage will depend on reaction parameters and the characteristics of the porous substrate. In addition, $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ Li ion battery electrodes on flexible metal foil were coated with Al_2O_3 ALD using the S-ALD reactor at 10-100 RPM. Initial coin-cell testing has demonstrated that enhanced capacity stability of these cathode electrodes is obtained after 2-5 Al_2O_3 ALD cycles.

9:40am **TF+EM+MI+MS-TuM6 Accurate Precursor and Reactant Delivery for Quantitative Atomic Layer Deposition**, ***Masafumi Kitano***, Stanford University, *M. Nagase, N. Ikeda*, Fujikin Incorporated, Japan, *P.C. McIntyre*, Stanford University

Atomic layer deposition (ALD) has been widely discussed in the literature from various points of view. Typically, the amount of the precursor and reactant supplied into the ALD chamber is dictated only by controlling valve operation time, and is not quantitatively defined. To achieve a more quantitative ALD process, we have developed new flow rate control system (FCS) which can accurately dose precursor and reactant into an ALD reactor. This FCS consists of an orifice plate, pressure sensor, thermal sensor, and piezo control valve. It can be heated to 250˚C to achieve sufficient vapor pressure for most precursors used in ALD of various inorganic compounds and elements. The FCS controls the flow rate under critical expansion conditions (or choked flow conditions); the flow rate through the orifice is proportional only to the upstream pressure of the orifice.[1,2] The piezo control valve accurately controls the upstream pressure and, thus, the flow rate. This mode of operation makes it possible to control the dosing of precursor and reactant by simply operating an endpoint valve placed close to the ALD reactor, because the upstream pressure is controllable whether the gas flow is running or not.

We have demonstrated an ALD process with trimethylaluminum (TMA) and water vapor (H_2O) reaction for Al_2O_3 deposition using the FCS to accurately control dosing into the ALD reactor. Excellent uniformity and reproducibility of deposition, and high quality dielectric properties of the resulting Al_2O_3 films have been achieved. The critical doses of TMA and H_2O into the chamber have been found to achieve surface saturating ALD of Al_2O_3 on a silicon substrate.

[1] A. Guthrie, R. K. Wakerling, “Vacuum Equipment and Techniques” McGraw-Hill book company, Inc., pp17, (1949)

[2] R. H. Perry, D. Green, “Perry's Chemical Engineers' Handbook, Sixth Edition” McGraw-Hill Co., pp5-14, (1984)

11:00am **TF+EM+MI+MS-TuM10 ALD for Capacitor Technologies**, ***Ramakrishnan Rajagopalan***, *C. Randall*, The Pennsylvania State University **INVITED**

Atomic layer deposition (ALD) is a powerful processing technique that can be used to modify interfacial processes occuring in electrochemical capacitors. Charge storage mechanism in electrochemical capacitors is either due to electrostatic double layer formation or pseudocapacitive faradaic interactions at electrode/electrolyte interfaces. The talk will present an overview of our efforts in developing pseudocapacitive vanadium oxide thin films using ALD approach on high surface area carbon electrodes. The deposition process is dependent upon the carbon properties such as surface functionalization and porosity. We will report our investigation of deposition of ALD films on nanostructured carbon electrodes with controlled porosity in mesopores (<20 nm) to ultramicropore (0.8 nm to 2 nm) ranges. ALD also facilitates the possibility of combining electrochemical effects with dielectric effects. ALD of dielectrics such as Al_2O_3 on electrodes used in aqueous, organic and lithium based electrolytes can mitigate the issues relating to electrochemical stability due to solvent decomposition reactions and leakage performance with limited effect on the ESR performance of the capacitor. There is also possibility of designing novel solid state capacitor structures that synergistically integrates the electrical double layer interactions due to ions with dielectric energy storage.

11:40am **TF+EM+MI+MS-TuM12 Compositionally and Functionally Graded Hybrid Layer for High-Performance Adhesion**, ***Yichuan Ding***, *R.H. Dauskardt*, Stanford University

Reliable bonding of organic/inorganic interfaces continues to be one of the most important challenges in multilayer devices including microelectronic, photovoltaic and display technologies. Hybrid molecular materials which contains both organic and inorganic components has been shown to be well suited for bonding organic/inorganic (metals, metal-oxides, nitrides, …) interface, mitigating moisture degradation and even stress migration. The hybrid films (less than 100nm) made of two primary precursors, an epoxysilane and a zirconium alkoxide, have been deposited via solution based synthesis, with low cost and high throughput. By optimizing sol-gel chemistry and processing conditions, we achieved an impressive tenfold improvement in interfacial adhesion at the epoxy/Si substrate interface, and have proven the suppression of moisture degradation at the interface.

In this work, we emphasized on our newly developed spray deposition technique with more versatility and better suited to large-scale manufacturing. We utilized both bilayer coating and dual-sources spray strategies to create highly compositionally and functionally graded hybrid film compared with films achieved via traditional dip-coating. XPS depth profiling shows highly graded hybrid films with independent compositional control within 80nm can be achieved via spray coating in the dry regime. We took advantage of the compositional control brought by spray coating to unravel the structure-property relationships in the multi-functional hybrid films by varying components/parameters to fine tune the molecular structure of the resulting film and relate that to its properties obtained from our advanced thin-film mechanical testing techniques together with other chemical characterization techniques (XPS, FTIR, NMR and GCMS). The evolution of the hybrid molecular network during film process and how molecular level details of the hybrid film has a large effect on its mechanical properties were better understood.

Vacuum Technology
Room: 230B - Session VT-TuM

Vacuum Suitcases and Particulate Control

Moderator: James Fedchak, NIST, Marcelo Ferreira, European Spallation Source

8:00am **VT-TuM1 Applications for Mobile Vacuum Environments in Semiconductor Manufacturing**, ***Daniel Babbs***, Brooks Automation **INVITED**

The majority of processes found in semiconductor manufacturing occur within a vacuum environment. A vacuum environment provides a stable operating regime which permits precise process control which is highly repeatable. However, after a semiconductor wafer is processed it is removed from the vacuum environment, placed into an atmospheric transport container and subsequently delivered to the next process tool. Transitioning the semiconductor wafer between atmospheric and vacuum environments has been the traditional process method in the industry but recent advancements in device structures below the 22nm technology node are challenging the effectiveness of this method. Specifically, management of the semiconductor wafer exposure limits to oxygen and moisture at all times is now becoming standard practice to achieve desirable production yields.

The application of a mobile vacuum carrier to transport and store semiconductor wafers provides a contiguous vacuum environment between process platforms. The vacuum carrier utilizes a standard mechanical interface, or vacuum port, for docking to the process platform and is compatible with current factory automation systems. The vacuum port provides automatic loading/unloading of the vacuum carrier which includes dynamic pressure equalization between source and target environments. Typically, a vacuum carrier load/unload on the vacuum port is completed in <60 seconds on average. Preliminary experiments have demonstrated acceptable vacuum performance sustained in the carrier over prolonged durations (after 72 hours <3 Torr). Over the same period, exposure limits of oxygen and moisture within the vacuum carrier are within part-per-million ranges (66ppm and 349ppm, respectively). The reduction in exposure to environmental contaminants removes variability thus improving process quality and yield. In addition, a mobile vacuum environment can be used to connect discrete process platforms and create customized process flows without the semiconductor wafers ever leaving vacuum. This capability presents opportunities to develop new equipment architectures and unique semiconductor processes.

In summary, as device dimensions continue to shrink, wafer sensitivity to environmental contamination increases. This in turn drives the necessity for improved environmental control throughout the entire semiconductor process including transport and storage of the semiconductor wafers. For semiconductor manufacturers, the mobile vacuum environment provides the capability for endpoint-to-endpoint control of the wafer environment not only within critical process chambers but also while transferring them between process platforms.

8:40am **VT-TuM3 Experience of UHV Transportation of Critical Components**, ***Paolo Michelato***, Italian National Institute for Nuclear Physics (INFN), Italy **INVITED**

High quantum efficiency semiconductor photocathodes, as alkali telluride and antimonides, are used as high brightness electron sources in laser triggered radio frequency and high voltage guns. These materials are quite sensitive to gas contamination and UHV conditions must be guaranteed during preparation, storage and handling. Their photo emissive characteristics, as the quantum efficiency, are strongly affected by the exposition to reactive gases as oxygen, carbon dioxide and water vapor.

Photocathodes are commonly prepared and fully characterized in the preparation laboratory and then moved to the point of use, usually inside the tunnel of the accelerator facility. Different laboratories built custom designed UHV suitcases, which will be described and analyzed in this paper, for the transportation and manipulation of these sensitive materials.

INFN Milano – LASA produces, handles and transports Cesium Telluride photocathodes to different laboratories since 1990. Our suitcases are successfully used for transferring photocathode between production sites (INFN Milano, DESY-HH, Fermilab) to the accelerator facilities at DESY Hamburg (FLASH, XFEL), DESY Zeuthen, FERMILAB and LBNL. Up to now, seven suitcases transfer photocathodes between laboratories for preparation procedure, use in the gun, diagnostic and post-mortem investigation.

The transportation of other critical and delicate components might benefit from a similar suitcase design.

Generally, a sputter ion pump maintains the photocathodes in UHV during their transfer. This type of pump is heavy, and needs a HV power supply for continuous operation. These characteristics pose serious limitations for cathode air freight transportation due to present safety regulation. To overcome these limitations, we adopt a different strategy coupling a NEG pump with sputter ion pump. With this approach the NEG pump can preserve photocathode characteristics for a long time, even with the sputter ion pump switched off.

At present, we are testing a SAES Getters NEXTorr® pump that combines, in a synergic design, sintered NEG and sputter ion pump technologies. This would provide a more compact and lightweight system, with less residual magnetic fringe field, and an integrated pressure reading. The paper will discuss the results so far obtained, in terms of suitcase performances and reliability as well as photocathode properties preservation.

9:20am **VT-TuM5 Particle Behavior in Vacuum Systems: Protection Schemes for EUVL Critical Surfaces, Speed Controlled Particle Injection, Prevention of Particle Formation during Pump Down***, D. Pui,* ***Shawn Chen***, University of Minnesota **INVITED**

Extreme Ultraviolet Lithography (EUVL) is a leading lithography technology for the next generation semiconductor chips. Photomasks, in a mask carrier or inside a vacuum scanner, need to be protected from nanoparticle contamination down to below 20 nm diameter, the minimum feature size expected from this technology. We have developed models and performed experiments in vacuum tools down to 20 mTorr. Nanoparticles between 60 nm and 250 nm were injected into the vacuum chamber with controlled speed and concentration to validate the analytical and numerical models. Also, methods and models were developed to evaluate nanoparticle generation, transport and deposition on photomasks in carriers. Various protection schemes have been developed and evaluated using these experimental and modeling tools. Inside the vacuum chamber, nanoparticles could be formed during rapid vacuum pump down and/or by conversion of outgassing materials by soft x-ray. The detection and control of these nanoparticle contaminants will also be addressed in this presentation.

11:40am **VT-TuM12 Differentially Pumped Interface to Transfer Environmentally Sensitive Materials Designed with Built-in figures of Merit***,* ***Hugo Celio***, University of Texas at Austin

An interface designed to transfer air sensitive samples (e.g., battery materials) from an argon filled glove box (1 part-per-million of O_2 and H_20) into an ultra-high vacuum (UHV) chamber for surface analysis is described. This interface (referred as interface for pressure-to-vacuum environmental sample transfer or IP-VEST) is equipped with a differentially pumped load lock, a buffer chamber, a detachable vacuum suitcase (referred to as a capsule), pump chamber, and a set of pressure gauges. Differential pumping minimizes back-flow from the mechanical pump that backs the turbomolecular pump (TMP) of the pump chamber. In the glove box, where argon pressure is 800-900 Torr, samples are loaded into the capsule and remain under this pressure during their transport to the load lock of the IP-VEST. An automatic sequence of pneumatic valves control differential pumping gas flow from the capsule to the pump chamber during the transition from atmospheric pressure (viscous flow) to high vacuum (molecular flow). During this pressure transition, the IP-VEST is also designed to generate a pressure spike in the buffer chamber that is a six order in magnitude, crossing over from the molecular flow to the viscous flow, and returning to molecular flow. This pressure spike is tunable with respect to pressure and time, and it is used as reference peak, allowing a comparison between pump down curves acquired during different sample transfer events. This pressure spike, combined with pump down curve, is referred to as a viscous-to-molecular flow curve (or spiked flow curve). The high repeatability of the spiked flow curves allows a user to develop a method, e.g., figures of merit, to evaluate sample transfer reliability during the entire transfer process that includes gaseous contents of an argon filled glove box and pumping efficiency of the IP-VEST. As a comparison, spiked flow curves were measured after filling the capsule near standard pressure from two sources of argon gas: (1) A high pressure cylinder bottle and (2) a commercial glove box. Both argon sources have intrinsic levels of $_2$ and H_2O at 1 ppm. In addition, silicon and tin were separately exposed to these two sources of argon in order to evaluate the amount of oxidation of these materials due to intrinsic and extrinsic (e.g., leaks and back-flow) factors. These samples were transferred using the IP-VEST that is coupled to a port of a UHV chamber which is equipped with an X-ray photoelectron spectroscopy (XPS). XPS confirms that the IP-VEST does not contribute to the oxidation of these materials due to extrinsic factors.

Exhibitor Technology Spotlight
Room: Hall 1 - Session EW-TuL

Exhibitor Technology Spotlight Session
Moderator: Dennis Sollon, Kurt J. Lesker

12:40pm **EW-TuL2 The Latest Developments in Surface Analysis from Thermo Fisher Scientific**, ***Tim Nunney***, Thermo Fisher Scientific, UK, *P. Mack, C. Deeks, R.G. White*, Thermo Fisher Scientific

Thermo Scientific offers a wide range of analytical techniques for materials characterisation, which include XPS, Raman, FTIR, EDS, WDS and EBSD. In this presentation we will discuss our latest developments in instrumentation and software to extend our capabilities for surface analysis.

1:00pm **EW-TuL3 EnviroESCA – The Revolution of a Method**, ***Andreas Thissen***, *S. Bahr, T. Kampen, O. Schaff*, SPECS Surface Nano Analysis GmbH, Germany

Since many decades XPS (or ESCA) is the well-accepted standard method for non-destructive chemical analysis of solid surfaces. To fulfill this task existing ESCA tools combine reliable quantitative chemical analysis with comfortable sample handling concepts, integrated into fully automated compact designs. Over the last years it has been possible to develop XPS systems, that can work far beyond the standard conditions of high or ultrahigh vacuum. Near Ambient Pressure (NAP) XPS has become a fastly growing field in research inspiring many scientist to transfer the method to completely new fields of application. Thus, by crossing the pressure gap, new insights in complicated materials systems have become possible using either synchrotron radiation or laboratory X-ray monochromators as excitation sources under NAP condtions. Based on this experience SPECS Surface Nano Analysis GmbH has developed a revolutionary tool to realize the long existing dream in many analytical laboratories: reproducible chemical surface analysis under any environmental condition. EnviroESCA allows for different applications, like extremely fast solid surface analysis of degassing (but also non-degassing) samples, ESCA analysis of liquids or liquid-solid interfaces, chemical analysis of biological samples, materials and device analysis under working conditions (in situ/in operando studies of catalysts, electrochemical devices etc.). Discover the new capabilities of EnviroESCA, a fully automated tool in a new sophisticated and compact design with uncompromising ease-of-use, and explore completely new fields of applications for the established analysis method XPS.

1:20pm **EW-TuL4 Latest Developments in XPS and Related Methods from Kratos Analytical**, ***Chris Blomfield***, *J.D.P. Counsell, S.J. Coultas, S.C. Page,* Kratos Analytical Limited, UK, *C. Moffitt*, Kratos Analytical Limited

The Axis Supra is the latest generation of XPS instrument from Kratos Analytical. In addition to offering enhanced energy resolution and sensitivity for XPS, it has a 15µm small area spectroscopy and 1µm imaging capability. The instrument is designed to offer a high level of flexibility and can be fitted with a range of complimentary surface analysis techniques such as UPS, ISS, AES, along with an additional surface science station and a range of sample treatment capabilities. In addition to offering benchmark level performance, the instrument and ESCApe data system combine to offer a high throughput platform optimised for the multiuser environment of today's surface analysis laboratory. Samples may pre-aligned and analyses predefined so that, when combined with the automated sample transfer capability, high levels of throughput can be achieved with unattended operation. Applications of high resolution imaging, multispectral imaging, gas cluster ion source and GCIS-UPS studies will be presented on a range of new materials to underline the leading capabilities of the Axis Supra.

1:40pm **EW-TuL5 What's New from Physical Electronics**, ***Scott Bryan***, Physical Electronics USA

What's New from Physical Electronics

2:00pm **EW-TuL6 AFM of Thin Films for Nanomechanical, Nanoelectrical, and Electromechanical Characterization**, ***Amir Moshar***, *A. Labuda*, Asylum Research, an Oxford Instruments Company

AFMs now offer characterization beyond just thickness, grain and domain sizes of thin films and coatings. Instrumentation advances enable hassle-free environmental experiments for studying solvent and thermal effects. Nanoelectrical, nanomechanical and electromechanical modes allow quantitative measurements of functional properties. AFMs are also faster, easier-to-use, and allow users a wider variety of such techniques enabling more meaningful, correlative results. In this presentation, Asylum Research will discuss the latest advances in AFM instrumentation, scan modes, and give real-world examples of research being done on the Cypher™ and MFP-3D™ AFMs. We'll also introduce the science behind making quantitative measurements of electromechanical response with interferometric AFM.

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 (≥ 31.5 Kω/□), 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 MoS_2 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 MoS_2 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.

Applied Surface Science
Room: 212D - Session AS+BI-TuA

Challenges in the Characterization of Polymer/Organic/ Biological Systems
Moderator: Bonnie Tyler, National Physical Laboratory (NPL), Jeffrey Fenton, Medtronic plc

2:20pm **AS+BI-TuA1 ASSD 30th Anniversary Lecture: 30 Years (ToF-)SIMS of Organic Materials: from Monolayer to 3D Microarea Analysis**, ***Birgit Hagenhoff***, Tascon GmbH, Germany **INVITED**

The presentation will follow the development track and the learning curve of (ToF)-SIMS for the characterization of organic materials.

Starting in the early 70s of the last century, when Alfred Benninghoven, based on research results for Ag catalyst samples, started into what would later become the wide-spread field of Static SIMS, the talk will cover the following areas

· Static SIMS: early beginnings

· Static SIMS: the importance of noble metal substrates

· Static SIMS: from quadrupoles to Time-of-Flight Analyzers

· Charge compensation: the gateway to bulk analysis

· Organic Imaging: limits of lateral resolution

· Cluster ion guns: getting sub-µm using Au and Bi LMIGs

· The road to organic depth profiling: SF_5^+ and C_{60}^+ sputtering

· Organic depth profiling: the use of Ar cluster ion sputtering

· 3D Microarea Analysis: Status-quo and challenges for the future

3:00pm **AS+BI-TuA3 Characterization of the Buried Interface between a Bacterial-Biofilm Resistant Coating and a Silicon Catheter by using Gas Cluster ToF-SIMS and Raman Microscopy**, ***Bonnie Tyler***, National Physical Laboratory (NPL), UK, *A.L. Hook, M.R. Alexander,* University of Nottingham, UK, *A. Giovannozzi,* INRIM, *A. Pelster, H.F. Arlinghaus*, University of Muenster, Germany

Thin film coatings are widely used in medical devices in order to improve the biological response to the device without compromising its mechanical performance. These coatings are frequently organic in nature and are applied to a wide range of substrate materials. The challenge of ensuring a stable linkage between the coating and the underlying substrate is common to all of these systems. Defects at the interface between the coating and the substrate can result in failure of the medical device with potentially serious consequences. The study of buried interfaces in organic systems, like those common in medical devices, has in the past been a nearly intractable problem because sputter depth profiling with monatomic ions destroys the relevant chemical information. Recent advances in Gas Cluster Ion Beam technology have opened up exciting possibilities to better understand these buried interfaces. In this work, we have studied adhesion between an bacterial-biofilm resistant polymer coating and an oxygen plasma-treated polymer surface using Argon Cluster 3D-imaging Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and Raman Microscopy. Analysis has been performed in both dry and hydrated state. The analysis provided several analytical challenges. Because the overlayer was not of uniform thickness, a depth scale correction was needed to reduce misleading artefacts at the interface. Analysis of the hydrated catheters required cryogenic analysis conditions. From the ToF-SIMS data we have been able to observe the presence of particles, cracks and water, and to monitor hydrophobic recovery at the interface between the coating and the catheter. Raman analysis has provided complementary information on the Van-Der-Waal interactions at the interface. The results have been compared to mechanical adhesion tests and help to provide a better understanding of the processes that influence adhesion between the coating and the catheter.

3:20pm **AS+BI-TuA4 How to Measure Reaction Rates on Surfaces?: Ambient Mass Spectrometry and XPS to Study the Rate of Organic Reactions on Functionalized Surfaces.**, *R. Sen, J. Escorihuela,* ***Han Zuilhof***, Wageningen University, Netherlands

Ultrathin coatings like self-assembled monolayers and polymer brushes have been used for a wide variety of studies and applications. Reactions within such monolayers or brushes are often difficult to follow, and their rates are typically not measurable: apart from a handful of cases in which electrochemical methods have been used, no rigorously measured kinetics on reactions within e.g. self-assembled monolayers are available. The current presentation will outline a generic approach, combining ambient mass spectrometry and XPS, to fill this gap, and provide a truly generic method to measure the rate of intramonolayer or intrapolymer organic reactions. Examples will include a variety of so-called click reactions, as these display a very high potential in materials science.

4:20pm **AS+BI-TuA7 Surface versus Bulk Chemistry of Reverse Osmosis Membranes**, ***Tamlin Matthews***, *R. Cieslinski, M. Paul, A. Roy*, The Dow Chemical Company

The polyamide layer of reverse osmosis (RO) thin-film composite membranes is ~100 nm thick. Separation of this thin layer from the supporting layers is a complex process and can only be done chemically, which results in a fragile polyamide layer and makes characterization challenging. X-ray photoelectron spectroscopy (XPS, near-surface) and Rutherford backscattering spectrometry (RBS, bulk) have been applied to characterize the polyamide layer, without the need to separate polyamide from the supporting layers. The combination of these methods allows the comparison of bulk vs. near-surface carboxylic acid content, which is a driver in RO performance. Additionally, elemental composition, thickness, and roughness of the RO membranes can be compared in systems with systematically changed monomers. This talk will focus on how the application of XPS and RBS can be used together for surface vs bulk chemical composition.

4:40pm **AS+BI-TuA8 Effect of Deep UV Irradiation on Polyester Family Polymers**, ***Lopamudra Das***, *M.J. Kelley*, College of William and Mary

In films and fibers, desired attributes of these polymers are often surface-mediated. Radical chemistry launched by deep UV offers attractive opportunities for surface modification, free of the environmental burdens of wet chemistry. We report the effect of 172 nm irradiation in the absence of oxygen on PET, PTT, PBT and PEN films, observed by FTIR, XPS and ToF-SIMS. Initial findings include carboxylic acid production and a loss of carbonyl carbon. To better understand surface reactivity, samples of each polymer were treated with silver trifluoroacetate or with heavy water.

5:00pm **AS+BI-TuA9 Going beyond State of the Art in SIMS Imaging in the Life-Sciences and for Organic Devices**, ***Ian Gilmore***, National Physical Laboratory, UK **INVITED**

In this celebratory 30th year of the Applied Surface Science Division, we can be sure that secondary ion mass spectrometry will feature strongly in the "Top-30" hit-parade. For example, SIMS, with its ability for high-sensitivity analysis has played an important role in the semiconductor industry measuring dopant profile concentrations. The rapid growth of the semiconductor industry is popularly summarised by Moore's law[1]; which shows that over the last five decades the number of transistors in a chip doubles every two years. Recently, Scannell et al[2] show that the reverse is the case for the pharmaceutical industry and the number of drugs per billion dollars of investment has dropped from around 50 to less than 1 over a similar timescale. They call this "Eroom's" law, Moore's law in reverse.

Analogously to the semiconductor industry, SIMS could now provide important benefits to the pharmaceutical industry. The challenge here is to measure where drugs go at the cellular level, even within specific organelles, to answer long-standing questions about whether drug concentrations are sufficiently high in the right places to have a therapeutic effect, or if the medicine is lodging within cellular components and causing toxicity. If anomalies were spotted earlier it might help to explain toxicities or lack of efficacy of a medicine and reduce costly late-stage failures. [3,4]

To meet this challenge, NPL in collaboration with GlaxoSmithKline, ION-TOF GmbH, Thermo Fisher Scientific and the University of Nottingham is building a revolutionary new instrument, the 3D nanoSIMS,[4] which incorporates the powerful Thermo Scientific™ Orbitrap™ mass analyzer for high-performance identification of drugs and metabolites. The stunning capability of SIMS to study drugs in tissue and cells will be highlighted and the characteristics of the new instrument will be outlined. The benefits of combining SIMS with the new generation of ambient mass spectrometry techniques and the rapidly rising challenge of Big Data will also be discussed.

References:

[1] Moore, Gordon E.. "Cramming more components onto integrated circuits" (PDF). Electronics Magazine. (1965)

[2] Scanwell, J.W., Blanckley, A., Boldon, H., Warrington B., Nat. Rev. Drug Discovery., 11, 191-99 (2012)

[3] C T Dollery, Clinical Pharmacology & Therapeutics, (2013); 93, 263–266.

[4] The 3D nanoSIMS project, http://www.npl.co.uk/news/3d-nanosims-label-free-molecular-imaging [2013 [http://www.npl.co.uk/news/3d-nanosims-label-free-molecular-imaging%20%5b2013]]

5:40pm **AS+BI-TuA11 Can *In Situ* Liquid SIMS Provide Enough Signals for Biology and Environmental Research?**, ***Zihua Zhu***, *Y. Zhou, X. Hua, J. Yu, J.E. Evans, D. Lao, X.-Y. Yu*, Pacific Northwest National Laboratory

In situ liquid SIMS is an R&D 100 award winner that was developed in PNNL since 2010. System for analysis at the liquid vacuum interface (SALVI) coupled with liquid SIMS has proven to be a promising new tool to provide molecular information at solid/liquid interfaces.[1,2] However, our initial data showed that signals of secondary positive ions were too low to be usable in some cases.[2,3] In addition, it was difficult to obtain strong negative molecular ion signals with m/z > 100.[2] These two drawbacks make SIMS community wonder the potential applications of this new analytical approach. In this presentation, we report that strong positive and negative molecular signals are achievable after we optimize the SIMS experimental conditions. Our results show that both beam current and primary ion species (e.g., Bi^+, Bi_3^+, Bi_3^{2+}) play important roles in achieving optimal molecular signals at the liquid interface. Data sets from three model systems, including an ionic liquid, water, and several liposome solutions, will be presented. In addition, beam damage at the liquid surface will also be discussed.

[1] B. Liu, X. Y. Yu, Z. Zhu, X. Hua, L. Yang, Z. Wang, *Lab Chip*, **2014**, *14*, 855.

[2] X. Hua, X. Y. Yu, Z. Wang, L. Yang, B. Liu, Z. Zhu, A. E. Tucker, W. B. Chrisler, E. A. Hill, S. Thevuthasan, Y. Lin, S. Liu, and M. J. Marshall, *Analyst*, **2014**, *139*, 1609.

[3] L. Yang, Z. Zhu, X. Y. Yu, S. Thevuthasan, J. P. Cowin, *Anal. Methods*,**2013**, *5*, 2515.

6:00pm **AS+BI-TuA12 Fundamental Metrology for Tissue Imaging by SIMS - A Study of Cholesterol and Determination of the Argon Cluster Sputtering Yield**, *P.D. Rakowska, M.P. Seah,* ***Rasmus Havelund***, *I.S. Gilmore*, National Physical Laboratory, UK

Secondary Ion Mass Spectrometry (SIMS) has become an invaluable tool to study organic and biological samples. An important biological application is in the analysis of mammalian cellular membranes. Considerable contribution to the field comes with the use of large cluster ion beams, and in recent years the application of argon gas cluster ion beam has emerged as the prevailing method.

Cholesterol, as a key component of nearly all mammalian cell membranes, is of particular interest. It alters the physical properties of the membranes, interacts with neighbouring lipids and proteins and is involved in numerous biomolecular processes. Being able to detect, identify and characterise the distribution of cholesterol in biological samples has vast implications in medical sciences. To do this, we need to underpin the basic metrology involved. It is important to evaluate cholesterol sputtering yields for argon cluster sputtering over a range of energy and cluster sizes so that a general description of the molecule behaviour may be established.

In this study, we compared the use of $C_{60}^{+(+)}$ and Ar_n^+ as sputtering ions for depth profiling of cholesterol thin films. Films of different thicknesses were prepared by thermal evaporation and the sputtering yields of cholesterol were measured from depth profiles made using 2.5 to 20 keV Ar_{1000}^+ and Ar_{5000}^+ and 10 and 20 keV $C_{60}^{+(+)}$ sputtering beams. We show that, at room temperature, the $C_{60}^{+(+)}$ ions caused significant damage but gave a well-behaved depth profile whereas Ar_n^+ gas clusters left the material undamaged but the very clean layer readily restructured making the profiles much more complex. This restructuring does not occur at room temperature normally but results from the actions of the beams in the sputtering process for profiling in SIMS. The sputtering yields from these restructured films are up to twice that for material not so restructured. Good profiles may be made by reducing the sample temperature. This is likely to be necessary for many lower molecular weight materials (below 1000 Da) to avoid the movement of molecules. The yields for both $C_{60}^{+(+)}$ and Ar_n^+ fit the universal yield equation [1]. Our results show that considerable differences can occur between the measurements performed with the two ion clusters, affected, in addition, by factors such as sample temperature or exposure to light. These will be discussed.

[1] M.P. Seah, J. Phys. Chem. C, 2013, 117 (24), pp 12622–12632

Biomaterial Interfaces
Room: 211D - Session BI-TuA

Cells and Microorganisms at Surfaces
Moderator: Axel Rosenhahn, Ruhr-University Bochum, Markus Valtiner, Max-Planck Institut für Eisenforschung GmbH

2:20pm **BI-TuA1 Control of Surface Physical Properties for Effectively Promoting and Maintaining Cell Clusters such as Stem Cell Colonies at Interfaces**, ***YingChih Chang***, *P.Y. Yeh*, Academia Sinica, Taiwan, Republic of China

A series of biomimetic polypeptide layer-by-layer conjugated supported lipid bilayers as lubricated thin films were constructed and characterized for their physical properties under cell-surface contact. The construct was used to promote the selection and maintenance of stem/progenitor cell colonies from the primary culture in one example, and to isolate circulating epithelial cells from human peripheral blood in another example. The adsorption of serum proteins, and nonspecifically bound cells are clearly reduced when a lipid coating was employed as the underneath layer, as studied by quartz-crystal microbalance with dissipation, and immunohistochemistry.

2:40pm **BI-TuA2 Immobilized Liquid Layers for Controlled Bacterial, Fungal, and Mammalian Cell Attachment**, ***Caitlin Howell***, *N. Juthani, N. MacCallum, Y. Kovalenko, S. Kelso, J. Lin, C. Nemr, P. Kim, J. Aizenberg*, Harvard University

Immobilized liquid layers, inspired by the *Nepenthes* pitcher plant, are emerging as a powerful new approach to the control of cellular attachment to surfaces. These layers present a "moving target" for the adhesion of fouling organisms and have shown promise as biofilm-resistant coatings. Tests on clinically-relevant bacteria and fungi such as *E. coli*, *S. aureus*, *S. epidermidis*, *P. aeruginosa*, and *C. albicans*, have shown significantly decreased adhesion without toxic effects. Immobilized liquid layers also show promise as tunable platforms for the attachment and detachment of mammalian cells, opening new directions in the area of tissue engineering. Finally, these surfaces can be made to be continuously self-replenishing through the incorporation of a bio-inspired vascular system, extending their longevity. We anticipate that these layers will prove a unique and adaptable platform for controlling the attachment of cells on surfaces.

3:00pm **BI-TuA3 Quantitative Characterization of Bacterial Cells Mixed with Nanoparticles**, *P.M. Martins, A.R. Silva,* University of Minho, Portugal, *I.M. Pinto, C. Sousa,* International Iberian Nanotechnology Laboratory, Portugal, *S. Lanceros-Méndez,* University of Minho, Portugal, ***Dmitri Petrovykh***, International Iberian Nanotechnology Laboratory, Portugal

The unique physicochemical properties of nanoparticles (NPs) are the basis for their potential applications in nanomedicine and biomedical research, whereby NPs interacting with cells provide a means for detecting, monitoring, or controlling cell functions via non-biological (magnetic, electronic, optical, mechanical) properties of NPs. When considering interactions of NPs with bacterial cells, the single-digit micrometer or even submicron sizes of typical bacteria have to be taken into account, in addition to their biological properties. For mixed suspensions of bacteria and NPs, therefore, both biological and physicochemical properties are involved in creating the corresponding micrometer- and nanometer-scale biointerfaces. While some methods are available for characterizing the biological properties of bacteria in suspension, reliable characterization of their physicochemical properties remains challenging, even for basic parameters, such as size distribution and concentration. *Staphyloccus aureus* bacteria are a convenient model system for developing and validating such physicochemical analysis of bacterial cells, due to their robust viability and nearly-spherical shapes with diameters of approximately 1 micrometer. We will describe the use of multiple complementary techniques, including flow cytometry, high-resolution microscopy, and optical spectroscopy, scattering, and absorption, for quantitative characterization of *S. aureus* suspensions and for extending these methods to investigations of NP-bacteria interactions.

3:20pm **BI-TuA4 Tethered Antimicrobial Peptide WLBU2 for Capture of Circulating Bacteria and Endotoxin in Sepsis**, ***Ramya Raman***, *K.F. Schilke*, Oregon State University

Severe sepsis is a blood infection that affects over 750,000 people each year in the US alone, killing 28-50% (more than prostate cancer, breast cancer and AIDS combined). Symptoms result from a highly dysregulated immune response, which, if untreated, can lead to multiple organ failure and death. Currently, treatment uses wide-spectrum antibiotics, but this is hindered by the rise of antibiotic-resistant 'superbugs'. One potential novel treatment is a high-throughput microfluidic hemoperfusion device, which specifically removes circulating bacteria and cell wall fragments ("endotoxin") from blood. A device with a biocompatible and bioactive surface coating could selectively bind circulating bacteria and endotoxins from blood, enabling rapid, safe treatment of bacterial sepsis. WLBU2 is an α-helical, cationic amphiphilic peptide (CAP) with 13 positively-charged arginine and 11 hydrophobic tryptophan/valine residues oriented on opposite faces of the helix. WLBU2 has high anti-microbial potency against a variety of pathogens, and integrates into bacterial cell membranes (Deslouches, et al. J. Antimicrob. Chemother. 2007; 60: 669-672). Biocompatible, non-fouling surfaces can be made by covalently tethering a dense brush of polyethylene oxide (PEO) polymer chains at the surface. Longer PEO tethers terminated with WLBU2 should enable increased mobility and solvent accessibility to tethered WLBU2, allowing it to bind bacterial cells, without compromising the biocompatibility of the coated surface. Poly-L-arginine and poly-L-Lysine served as controls for charge effects, and Cys-WLBU2 served as a tether-free control. The surface chemistry is consistent with peptide immobilization at the surface using X-ray Photoelectron Spectroscopy (XPS). Atomic Force Microscopy (AFM) images demonstrated the uniform coverage of gold surfaces with PEO and peptides. Scanning Electron Microscopy (SEM) and Quartz Crystal Microbalance with Dissipation (QCMD) were used to demonstrate capture of bacteria at the coated surfaces. Tethered WLBU2 may more effectively bind P. aeruginosa than surface-bound WLBU2. Future work will focus on optimization of the coating to enable high loading of tethered bioactive molecules, without compromising surface biocompatibility. We are also developing a novel surface coating platform, using self-assembly and immobilization of PEO-based surfactants. This method shows promise in providing biocompatibility and biological function to a variety of polymers used in medical devices, without requiring expensive and toxic crosslinking reagents.

4:20pm **BI-TuA7 Concentration Dependent Acceleration of hMSC Differentiation on Orthogonal Concentration Gradients of RGD and BMP-2 Peptides**, ***Matthew Becker***, The University of Akron **INVITED**

Self-assembled monolayer substrates containing tethered orthogonal concentration profiles of GRGDS and BMP-2 peptides are shown to synergistically accelerate the proliferation and osteoblastic differentiation of human mesenchymal stem cell (hMSC) populations *in vitro* without the use of osteogenic additives. Concurrently, the single peptide gradient controls (RGD or BMP-2 only) were found to induce significantly different proliferation and differentiation behavior from the orthogonal substrates. hMSC cells were individually isolated for qPCR at specified points along the gradients using laser capture microdissection. Bone sialoprotein (BSP) and Runt-related transcription factor 2 (Runx2) qPCR data corresponded spatially and temporally to protein marker data obtained from immunofluorescent imaging tracking the differentiation process. Genomic and protein data at high concentrations of both BMP-2 (25 pmol/cm^2) and GRGDS (71~83 pmol/cm^2) were shown to have a cooperative acceleration on the hMSC differentiation timeline relative to the individual peptide concentrations. These data highlight the utility of the orthogonal gradient approach to help identify the synergistic concentrations of peptides and growth factors that can be advanced in translationally relevant systems.

5:00pm **BI-TuA9 How Does Plasma Surface Modification Affect Biological Responses?**, ***Adoracion Pegalajar-Jurado***, *M.J. Hawker, M.N. Mann, E.R. Fisher*, Colorado State University

Biofouling causes severe and costly problems in industries including, but not limited to water filtration, food packaging and preservation, marine operations and biomedical devices. Depending on the industrial context, the term biofouling assumes different meanings including bacterial attachment and biofilm formation, undesired protein adsorption, or prevention of cell growth and tissue regeneration. Nevertheless, the process commences with undesired interactions of biological agents with the material surface.Consequently, the ability to tune surface properties to tailor biological response highlights an exceptional route towards preventing issues associated with biofouling. Although surface micro- and nanotopography, surface free energy, and surface chemistry are known to affect biological agent-surface interactions, this presentation will focus specifically on the effects of surface chemical modifications of 3D constructs (i.e. drug delivery systems and polymeric membranes and scaffolds) on biological responses. Among others, plasma surface modification offers a tunable and versatile parameter space for tailored and reproducible surface modification while retaining the morphology of the material, to produce *bio-nonreactive materials* (limit bacterial and cell attachment and low cytotoxicity). On 2D substrates, plasma polymerized cineole films have demonstrated limited *Escherichia coli* (*E. coli*) attachment over 18 hours and non-cytotoxic to mammalian fibroblast .[1] Herein, such films were used to conformally encapsulate 3D constructs. Results from both *E. coli* attachment studies as well as cytotoxicity studies will be presented. Alternatively, allylamine/allyl alcohol plasma copolymerized films applied to 3D materials and water plasma treated nitric-oxide releasing materials will be included as *bio-reactive* materials. In this case, human dermal fibroblast attachment and growth was enhanced in comparison to unmodified materials. Through these model systems, we will explore the use of plasma surface modification to minimise fouling and/or enhance biocompatibility of a 3D material resulting in the extension of device lifetime, and enhancement of performance.

Keywords: plasma surface modification, bio-reactive, bio-nonreactive

[1] Pegalajar-Jurado, A., Easton, C. D., Styan, K. E., McArthur, S. L., Journal of Materials Chemistry B, 2, no. 31 (2014): 4993-5002.

5:20pm **BI-TuA10 Stereoscopic Tracking Reveals Responses of Barnacle Larvae to Surface Cues**, *S. Maleschlijski, G.H. Sendra, S. Bauer,* Karlsruhe Institute of Technology (KIT), Germany*, A. Di Fino,* Newcastle University, UK*, L. Leal-Taixe,* Leibnitz University Hannover, Germany*, T. Ederth,* Linköping University, Sweden*, N. Aldred,* Newcastle University, UK*, B. Liedberg,* NTU Singapore*, A.S. Clare,* Newcastle University, UK*, B. Rosenhahn,* Leibnitz University Hannover, Germany*,* ***Axel Rosenhahn***, Ruhr-University Bochum, Germany

The critical step in surface colonization by marine biofouling organisms is surface exploration and settlement of the sessile stages (larvae, spores). Barnacles are one of the most important biofouling organism and surface selection of their larvae is a highly selective process [1]. 3D stereoscopic tracking enables quantitative analysis of the pre-settlement behavior and thus to understand how larvae respond to chemical and physical surface cues. We developed a transportable, submersible stereoscopic system which can be applied to record three dimensional video data and to extract swimming trajectories of multiple, label-free objects. The pre-settlement ritual can be classified in different motion patterns which vary in characteristic parameters, such as distance to the surface, velocity, or the curvature of the motion [2]. In general the larvae favor both, liquid-solid and liquid-air interfaces. The distribution within the water column and the fraction of larvae exploring the solid surface is determined by its chemistry. Using different self assembled monolayers we found a positive correlation of the settlement probability with both, the fraction of larvae exploring the interface and their mean swimming velocity [3]. Thus, 3D tracking provides a predictor for settlement probability. A combination of stereoscopic tracking with imaging surface plasmon resonance reveals that a temporary adhesive is an important ingredient in the mechanosensing process. Surfaces with high settlement probability and low swimming speeds tend to bind the adhesive stronger than the sensory setae while inert surfaces with low settlement probability and high swimming speeds interact only very weakly.

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[2] S. Maleschlijski, S. Bauer, A. DiFino, H. Sendra, A.S. Clare, A. Rosenhahn, J. Roy. Soc. Interf. 2014, 12(102), 20141104

[3] S. Maleschlijski, S. Bauer, A. Di Fino, G.H. Sendra, A.S. Clare, A. Rosenhahn, Biofouling 2014, 30(9), 1055

5:40pm **BI-TuA11 New Materials Toolboxes for Tissue Engineering and Regenerative Medicine Applications**, ***Adam Celiz****, Harvard University*, J. Smith,* University of Nottingham, UK*, A. Patel, R. Langer, D. Anderson,* Massachusetts Institute of Technology*, D. Mooney,* Harvard University*, L. Young, M. Davies, C. Denning, M.R. Alexander*, University of Nottingham, UK

A key hurdle in translating stem cell therapies from research to industrial scale and clinical application is to produce the necessary numbers of cells in xeno-free, defined culture systems. For example, a heart attack can cause a loss of 1 billion cardiomyocytes and similar cell numbers are lost during progression of other conditions such as multiple sclerosis and diabetes. To meet the demand for such high cell numbers, materials scientists have been challenged to discover new synthetic biomaterials as xeno-free growth substrates.[1] We apply a high throughput materials discovery approach to identify a novel polymer for hPSC culture using microarray screening of an unprecedented chemical space (141 monomers, polymerized alone and mixed to form 909 unique polymers, tested in 4356 individual assays). This identified the first synthetic polymeric substrate that achieves both pluripotent hPSC expansion (in the commercially available defined culture media, StemPro and mTeSR1) and subsequent multi-lineage differentiation into representatives of the three germ layers, namely cardiomyocytes, hepatocyte-like cells and neural progenitors.[2] Surface analysis techniques such as ToF-SIMS and XPS were used to identify chemical moieties at the biomaterial interface that contributed to maintaining hPSC pluripotency. The identification of these controlling surface moieties was essential in the

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*** BID Early Career Researchers Award**

development of a facile scale up procedure from arrayed spots to coated cultureware that can be used *off-the-shelf*.

An alternative strategy for cell and tissue regeneration is to harness the natural regenerative capacity of the human body through activation of quiescent cell populations. Biomaterials such as hydrogels that mimic native extracellular matrix can be synthesized and implanted *in vivo* to present biophysical and biochemical cues to their surroundings and activate/traffic these cell populations towards a desired therapeutic effect.[3] Novel bioactive hydrogels, synthesized through bioorthogonal click chemistry methods, will be presented that can activate and regulate quiescent cell populations to aid regeneration of lost tissue after trauma or injury. The utility of these new materials will be demonstrated through muscle regeneration in a hind limb ischemia mouse model.

1. A. D. Celiz *et al.* Nat. Mater. (2014) *13*, 570.
2. A. D. Celiz *et al.* Adv. Mater. ***in press*** adma.201501351R1.
3. C. A. Cezar *et al.* Adv. Drug Deliv. Rev. (2014) http://dx.doi.org/10.1016/j.addr.2014.09.008.

Electronic Materials and Processing
Room: 210E - Session EM+MN+PS-TuA

More than Moore: Novel Approaches for Increasing Integrated Functionality

Moderator: Andy Antonelli, Nanometrics, Sean King, Intel Corporation

2:20pm **EM+MN+PS-TuA1 Maintaining the Pace of Progress as we Approach the end of Moore's Law: *Heterogeneous Integration, New Materials, New Processes, New Architectures, Bill Bottoms***, 3MTS **INVITED**

The environment is rapidly changing as we approach the end of Moore's Law scaling. Scaling continues but benefits in performance, power and cost are reduced. At the same time drivers for the electronics industry are impacted by the emerging Internet of Things and Migration to the Cloud. Satisfying the requirements of these emerging drivers cannot be accomplished with the current technology. It will require innovative heterogeneous integration approaches to satisfy demands for power, latency, bandwidth, reliability and cost in an environment where transistors will wear out.

Overcoming the limitations of the current technology will require heterogeneous integration using different materials, different device types (logic, memory, sensors, RF, analog, etc.) and different components incorporating multiple technologies including electronics, photonics, and MEMS in new, 3D, system-in-package (SiP) architectures. New materials, manufacturing equipment and processes will be required to accomplish this and meet the market demand for continuous reduction in cost per function.

The requirements, difficult challenges and potential solutions will be discussed.

3:00pm **EM+MN+PS-TuA3 More than Moore - Wafer Scale Integration of Dissimilar Materials on a Si Platform**, ***Thomas Kazior***, *J. LaRoche*, Raytheon Company **INVITED**

Advances in silicon technology continue to revolutionize microelectronics. However, Si cannot do everything, particularly for high performance, high frequency RF and mixed signal applications. As a result circuits based on other materials systems, such as III-V semiconductors, are required. However, these other device technologies do not enjoy the integration density, cost benefit and manufacturing infrastructure of Si. So how can we get the 'best of both worlds'? What is the best way to integrate these dissimilar materials with Si? In this paper, we review different heterogeneous integration approaches and summarize our results on the successful wafer-scale, 3D heterogeneous integration (3DHI) of GaN HEMTs and Si CMOS.

Our Au-free GaN HEMTs have been successfully fabricated entirely in a Si foundry on semi-standard, 200 mm diameter Si wafers using Cu damascene interconnects. RF performance compares favorably with GaN on SiC devices fabricated in a III-V foundry with Au-based contact and interconnect metallurgy. Oxide bonding is being used to integrate these GaN on Si wafers with Si CMOS wafers. Through-dielectric-vias (TDVs) are used to interconnect the high performance GaN RF devices/circuits with high density CMOS control and logic circuits, resulting in ultra-short, wide-bandwidth interconnects enabling circuit optimization through intimate and arbitrary placement of CMOS logic and control circuitry relative to III-V devices. Through-substrate-vias (TSVs) are used for thermal management.

This 'flexible' wafer-scale, integration platform is compatible with other III-V devices, other (non-Si) device/component technologies and any node of Si CMOS or SiGe BiCMOS. The 3DHI process is being used to fabricate cost effective, high performance, digitally enhanced, RF and mixed signal ICs such as 'intelligent' and adaptive/reconfigurable transceivers.

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_2O_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.

Exhibitor Technology Spotlight
Room: Hall 1 - Session EW-TuA

Exhibitor Technology Spotlight Session

4:00pm **EW-TuA6 High Efficiency, High Capacity and Economical "Point of Use" Gas Abatement**, ***D.K. Prasad***, CS CLEAN SYSTEMS, Inc.

Air pollution regulations, employee health concerns and growing awareness of toxic agents from semiconductor, industrial and research facilities demand improvements in exhaust gas conditioning. The NOVASAFE dry scrubber reduces the hazards associated with pyrophoric, toxic and corrosive gases and vapors. NOVASAFE effluent gas scrubbers offer an extremely safe and efficient way to treat such process exhausts. The scrubber is a technologically advanced device, containing approximately 10 liters of granulate scrubbing media specific to the process chemistry, and can be used in both production and laboratory and research environments. Operating passively at room temperature, the granulate material reacts on contact with process gases and chemically converts them to non-volatile inorganic solids. NOVASAFE, with its compact form factor, can be integrated with your vacuum pump system to provide a minimal footprint solution. Effluent is abated to sub-TLV levels. The NOVASAFE requires no preventative maintenance, and is replaced and disposed of at its end of life. Granulate is available for many different chemistries, including hydrides, acid gases, metalorganics, etc. making NOVASAFE a cost-effective solution for etch, MOCVD, ALD, ion implant and many other applications.

IPF on Mesoscale Science and Technology of Materials and Metamaterials
Room: 210F - Session IPF+MS-TuA

Frontiers in Physics
Moderator: Jim Hollenhorst, Agilent, Cathy O'Riordan, AIP

2:20pm **IPF+MS-TuA1 Giving New Life to Materials for Energy, the Environment and Medicine**, ***Angela Belcher***, MIT Koch Institute for Integrative Cancer Research **INVITED**

Organisms have been making exquisite inorganic materials for over 500 million years. Although these materials have many desired physical properties such as strength, regularity, and environmental benign processing, the types of materials that organisms have evolved to work with are limited. However, there are many properties of living systems that could be potentially harnessed by researchers to make advanced technologies that are smarter, more adaptable, and that are synthesized to be compatible with the environment. One approach to designing future technologies which have some of the properties that living organisms use so well, is to evolve organisms to work with a more diverse set of building blocks. The goal is to have a DNA sequence that codes for the synthesis and assembly of any inorganic material or device. We have been successful in using evolutionarily selected peptides to control physical properties of nanocrystals and subsequently use molecular recognition and self-assembly to design biological hybrid multidimensional materials. These materials could be designed to address many scientific and technological problems in electronics, military, medicine, and energy applications. Currently we are using this technology to design new methods for building batteries, fuel cells, solar cells, carbon sequestration and storage, enhanced oil recovery, catalysis, and medical diagnostics and imaging. This talk will address conditions under which organisms first evolved to make materials and scientific approaches to move beyond naturally evolved materials to genetically imprint advanced technologies with examples in lithium ion batteries, lithium-air batteries, dye-sensitized solar cells, and ovarian cancer imaging.

3:00pm **IPF+MS-TuA3 XFEL Movies of Molecular Machines at Work**, ***John Spence***, Arizona State University **INVITED**

With about 1E12 coherent hard X-ray photons per shot of 10 fs duration at 120 Hz, the invention of the X-ray laser (XFEL) has provided many new research opportunities for stuctural biology, which I will review. Our first discovery, that these pulse are so brief that they outrun radiation damage, so that damage-free diffraction patterns at atomic resolution and femtosecond time resolution can be recorded to make movies of protein function, has proved immensely fruitful. Other advances in solution scattering, analysis of protein nano crystals, and imaging of single particles which cannot easily be crystallized, such as viruses, wll be also be reviewed. This work forms part of the activity of the NSF's BioXFEL STC, a consortium of seven US campuses devoted to the use of XFELs for Biology. (http://www.bioxfel.org).

4:20pm **IPF+MS-TuA7 Frontiers of Ocean Sensing**, ***Susan K. Avery***, Woods Hole Oceanographic Institution **INVITED**

The ocean accounts for more than two-thirds of Earth's surface and is our planet's largest biome, yet remains largely unexplored. Because seawater is opaque to most wavelengths of electromagnetic radiation, all but a few centimeters of the upper ocean are invisible to satellites. As a result, only about 5 to 15 percent of the seafloor is mapped in any detail and much of the water column has not been explored. Many of the transient phenomena that occur on, in, or above the ocean—and across a wide range of spatial and temporal scales—have been extremely difficult to capture, and even more difficult to monitor over long periods. New technologies and new adaptations of existing technologies, however, are opening the ocean in all its complexity to researchers at sea and on shore. Our challenge now is to take advantage of these innovations in sensing and observing, not only to fully grasp the role that the ocean plays in making Earth habitable, but also how it fits into planetary and societal changes that are taking place before our very eyes.

5:00pm **IPF+MS-TuA9 New States of Electronic Matter and their Potential for Science and Computation**, ***Joel Moore***, University California, Berkeley **INVITED**

A major development in solid-state physics over the past decade is the discovery of several new classes of electronic materials that combine features of metals and semiconductors in novel and potentially useful ways. "Topological insulators" are materials that insulate in bulk but have atomically thin conducting layers at their surfaces as a subtle consequence of spin-orbit coupling. "Weyl" and "Dirac" semimetals are three-dimensional materials that realize two different 3D generalizations of the massless electronic structure of graphene, a single layer of carbon atoms, whose discovery was recognized by the 2010 Nobel Prize. We explain the origin of these materials and how they might enable dissipationless electrical conduction and superconducting states with fractional "Majorana" particles.

5:40pm **IPF+MS-TuA11 The Universe in Motion: Listening to Gravitational Waves with LIGO**, ***Michael Zucker***, Massachusetts Institute of Technology **INVITED**

Almost 100 years ago, Einstein showed that traces of matter and energy's gyrations are continuously broadcast throughout the universe, in the form of *gravitational waves:* ripples in the underlying geometry of space. Fresh from a major upgrade, the Laser Interferometer Gravitational-wave Observatory (LIGO) is now poised to detect and decode these broadcasts, opening a new era of physics and astronomy. I will talk about why LIGO is so different from other observatories, and describe some of the daunting technological challenges we've overcome to help us realize Einstein's vision.

In-Situ Spectroscopy and Microscopy Focus Topic
Room: 211C - Session IS+AS+SS-TuA

Environmental TEM Studies for Catalytic and Energy Materials
Moderator: Franklin (Feng) Tao, University of Kansas, Judith Yang, University of Pittsburgh

2:20pm **IS+AS+SS-TuA1** ***In Situ* and *Operando* TEM of Thermal and Photocatalysts**, ***Peter Crozier***, *B.K. Miller, L. Zhang, Q. Liu*, Arizona State University **INVITED**

Heterogeneous catalysts play a vital role in the development of energy technologies. Understanding the fundamental relationships between catalyst activity and structure at the nanoscale will enable the improved design of catalyst nanostructures. *In-situ* and *operando* environmental transmission electron microscopy (ETEM) is a powerful technique for the investigation of structure-reactivity relationships in high surface area catalysts under reaction conditions. With current instruments, atomic resolution imaging and spectroscopy can be carried out in the presence of gas, liquid, light and thermal stimuli. The combination of mass spectrometry and electron energy-loss spectroscopy allow catalytic products to be detected and quantified directly in the electron microscope. Several specific applications of ETEM instrumentation and experiments to several heterogeneous catalysts will be presented.

Photocatalytic water splitting can be accomplished by a heterostructure of several materials, including a light absorbing semiconductor and one or more co-catalysts. Our group has focused on Ni-NiO co-catalysts on both TiO_2 and Ta_2O_5. In the Ni-NiO/TiO_2 system, deactivation occurs due to this Ni dissolution into water during illumination and H_2 is only produced by the oxidation of Ni metal[1]. For the Ta_2O_5 supported catalyst, H_2 was produced predominantly by a catalytic reaction [2] and the deactivation rate was found to be inversely proportional to the initial thickness of the NiO shell. In both systems, deactivation is observed only during light illumination, so that this deactivation is properly called photocorrosion.

Our group has also been pioneering the use of operando TEM to study CO oxidation over supported Ru nanoparticles [3]. There is uncertainty and debate in the literature regarding the most active form of this catalyst. Images of the Ru nanoparticles after reduction *in-situ* show a clean metal surface, but after only 0.5% O_2 is introduced into the cell, a thin oxide layer forms on the surface. Similar experiments are currently being performed under operando conditions.

References:

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3:00pm **IS+AS+SS-TuA3 Environmental TEM Study of Gold and Platinum Nanoparticulate Catalysts**, *H. Yoshida, Y. Kuwauchi, H. Omote*, ***Seiji Takeda***, Osaka University, Japan **INVITED**

The catalytic activity of metal nanoparticles depends on their size, shape, and surface structure. It is well-known that the adsorption of gases induces changes in the shape and surface structure of metal nanoparticles. Thus, it is important to obtain structural information about metal nanoparticles under reaction conditions to elucidate the correlation between the catalytic activity and the morphology of the nanoparticles. Environmental transmission electron microscopy (ETEM) is one of the powerful methods for the study of catalytic materials under reaction conditions at atomic scale [1]. In this study, we have investigated the shape and surface structure of Au and Pt nanoparticles that are supported on CeO_2 in reactant gases by a Cs-corrected ETEM.

We have found that the surface structure of a Au nanoparticle was reconstructed during CO oxidation at room temperature [2]. The {100} facets remain unreconstructed in vacuum. Under CO oxidation reaction conditions, the Au atomic columns on the topmost and second topmost {100} layers shift to peculiar positions. In the reconstructed surface the Au atoms on the topmost surface layer form an undulating hexagonal lattice, while those on the second topmost surface layer form a normal square lattice with slight distortion. This atomic-scale *in-situ* visualizing method provides us with insights into reaction mechanisms in heterogeneous catalysis.

We have observed the oxidation and reduction processes of the surface of Pt nanoparticles by ETEM. Atomic layers of Pt oxide were formed gradually in O_2 at room temperature during ETEM observations. In situ atomic resolution ETEM, combined with in situ electron energy-loss spectroscopy, showed that atomic layers of Pt oxides, including α-PtO_2 and Pt oxides of other forms, first started forming on the preferential facets of Pt nanoparticles at the early stage, entire oxidization on the whole surface of Pt nanoparticles then followed. The oxides were reduced promptly to Pt by adding a small amount of CO or H_2O vapor to the dominant O_2 gas. It is concluded that electron irradiation during ETEM observation activates the gases non-thermally, therefore promoting or suppressing the processes at room temperature [3].

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4:40pm **IS+AS+SS-TuA8 Environmental Study of the Reaction-driven Restructuring of Ni-Co Bimetallic Nanoparticles**, *C.S. Bonifacio,* University of Pittsburgh*, H.L. Xin,* Brookhaven National Laboratory*,* ***Sophie Carenco****, M.B. Salmeron,* Lawrence Berkeley National Laboratory*, E. Stach,* Brookhaven National Laboratory*, J.C. Yang*, University of Pittsburgh

Bimetallic nanoparticles (NPs) possess novel catalytic, optical, and electronic properties compared to their monometallic counterparts. These catalytic properties can be controlled by fine-tuning the NP structure and dimension, surface oxidation, and chemical composition. For instance, bimetallic NPs with a core-shell structure can allow for fine tuning of reactivity, averting sintering issues in the core, and even increase tolerance to high temperature exposure. Above all, elemental segregation in the core-shell structure has been demonstrated as a potential route of modifying the NPs catalytic properties through *in situ* gas reaction studies. To confirm this hypothesis, we have used *in situ* imaging and spectroscopy techniques to study Ni-Co core-shell NPs under environmental conditions to provide direct evidence of elemental redistribution during reaction . Two pairs of oxidation and reduction reactions were performed in an environmental transmission electron microscope (ETEM) at 0.3 Torr in O_2 and H_2 gas at 220°C and 270°C, respectively. Electron diffraction patterns and electron energy loss spectroscopy (EELS) maps showed a reaction-driven restructuring of the core-shell NPs with Ni species migrating to the NP surface by the 2nd reduction cycle. These results are in agreement with previous ambient-pressure x-ray photoelectron spectroscopy (AP-XPS) studies of the same NPs under identical reaction conditions. Furthermore, the ETEM results confirm the NP structure without erroneous interpretations that may result from post-mortem analysis of the samples. Quantitative analysis of the EELS results is underway to identify the valence states during the oxidation-reduction reactions. Correlation of the reaction-driven restructuring of NPs with the electronic structure changes from ETEM and AP-XPS will be provide insight into the optimum reaction conditions, i.e., catalytic properties, of the Ni-Co core-shell NPs in challenging reactions such as selective CO_2 reduction.

5:00pm **IS+AS+SS-TuA9 *In situ* Vibrational Spectroscopy Investigation of the Surface Dependent Redox and Acid-base Properties of Ceria Nanocrystals**, ***Zili Wu***, Oak Ridge National Laboratory **INVITED**

Ceria is best known for its excellent redox property that makes it an important component in the three-way catalyst for auto exhaust cleanup. This is a result of its high oxygen storage capacity associated with the rich oxygen vacancy and low redox potential between Ce^{3+} and Ce^{4+} cations. Equally interesting yet less is known about ceria is its versatile acid-base properties. Either as a standalone catalyst, a modifier or a support, ceria and ceria-based catalysts can catalyze the transformation of a variety of organic molecules that makes use of the acid-base as well as the redox properties of ceria.

Recent advances in nanomaterials synthesis make it possible to achieve nanocrystals with crystallographically defined surface facets and high surface area, which can be considered as ideal model systems for catalytic studies under realistic conditions. In this work, I will showcase how we can make use of ceria nanoshapes as model systems to gain molecular level understanding of the shape effect on both redox and acid-base properties and catalysis of ceria nanocrystals *via in situ* IR and Raman spectroscopy. Insights have been gained into how the surface structure of ceria catalyst affects profoundly its redox and acid-base properties and consequently the catalytic behaviors. It is suggested that the surface structure of ceria controls the catalytic performance through the combination of various factors including structure-dependent surface sites geometry, lattice oxygen reactivity, surface vacancy formation energy, defect sites, and acid-base property on ceria.

Acknowledgements: This work was supported by Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy. A portion of the work was supported by the Center for Understanding & Control of Acid Gas-Induced Evolution of Materials for Energy (UNCAGE-ME), an Energy Frontier Research Center funded by DOE, Office of Science, Basic Energy Sciences. The IR and Raman work were conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

5:40pm **IS+AS+SS-TuA11 Direct Writing of sub-10 nm Structures from Liquid with Helium Ions**, *V. Iberi, R.R. Unocic,* ***Nathan Phillip****, A. Belianinov, A.J. Rondinone, D.C. Joy, O.S. Ovchinnikova*, Oak Ridge National Laboratory

In-situ direct writing by electron beam from solutions opens a pathway for resistless fabrication of nanostructures at high throughput. However, when using electrons to direct write in solution the minimal size of the created structures is limited to the micron scale due to fundamental physics of the interactions between the electron beam and the liquid, including the lateral transport of solvated electrons and ionic species. Use of the helium beam with the opposite charge and shorter mean free path offers the potential for the localization of the reaction zone on the single digit nanometer scale. Here we will present our results demonstrating writing of platinum structures from liquid (beam induced electroplating) in a platinum chloride solution using helium ions with sub-10 nm resolution. Using data analytics on acquired in-situ growth movies we are able to elucidate the main statistical descriptors for helium ion beam initiated platinum structure growth. The possible mechanisms of beam induced growth and ultrahigh localization of reaction zone are discussed. Furthermore, we will discuss optimization of solution chemistry and instrumental parameters as they relate to the quality and thickness of structures and the extension to device fabrication on a single digit nanometer level.

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

Magnetic Interfaces and Nanostructures
Room: 230A - Session MI+SA-TuA

Spin Currents, Spin Textures and Hybrid Magnetic Structures
Moderator: Greg Szulczewski, The University of Alabama

2:20pm **MI+SA-TuA1 Spin Hall Effect in Metallic Multilayers**, ***Georg Woltersdorf***, Martin Luther University Halle-Wittenberg, Germany, *M. Obstbaum, M. Decker, D. Wei, C.H. Back*, University of Regensburg **INVITED**

The discovery of the spin pumping effect and the Spin Hall Effect (SHE) has stimulated the research on dynamics in metallic magnetic nanostructures. Here a comprehensive study of the SHE in metallic multilayers will be presented. We study the direct as well as the inverse SHE. In the case of the direct SHE a dc charge current is applied in the plane of a ferromagnet/normal metal layer stack and the SHE creates a spin polarization at the surface of the normal metal leading to the injection of a spin current into the ferromagnet [1,2]. This spin current is absorbed in the ferromagnet and causes a spin transfer torque. Using time and spatially resolved Kerr microscopy we measure the transferred spin momentum and compute the spin Hall angle. In a second set of experiments using identical samples pure spin currents are injected by the spin pumping effect from the ferromagnet into the normal metal [3]. The spin current injected by spin pumping has a large ac component transverse to the static magnetization direction and a very small dc component parallel to the magnetization direction. The inverse SHE converts these spin current into charge current [4,5]. The corresponding inverse SHE voltages induced by spin pumping at ferromagnetic resonance (FMR) are measured in permalloy/platinum and permalloy/gold multilayers in various excitation geometries and as a function of frequency in order to separate the contributions of anisotropic magnetoresistance and SHE. In addition, we present experimental evidence for the ac component of inverse SHE voltages generated by spin pumping [6,7].

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3:00pm **MI+SA-TuA3 Chiral Spin Textures in Ultrathin Ferromagnets**, ***Geoffrey Beach***, Massachusetts Institute of Technology **INVITED**

Spin orbit coupling at interfaces in ultrathin magnetic films can give rise to chiral magnetic textures such as homochiral domain walls and skyrmions, as well as current-induced torques that can efficiently manipulate them [1-3]. This talk will describe the statics and dynamics of chiral spin textures in thin-film nanowires stabilized by the Dzyaloshinskii-Moriya interactions (DMI) at a heavy metal/ferromagnet interface. We show that the DMI depends strongly on the heavy metal, differing by a factor of ~20 between Pt and Ta [2], and describe the influence of strong DMI on domain wall dynamics [1,2] and spin Hall effect switching [3]. We present high-resolution magnetic imaging of static magnetic textures that directly reveal the role of DMI and allow its strength to be quantified [4]. Finally, we will describe how a gate voltage can be used to control interfacial magnetism and magnetic domain walls in nanowires by manipulating interfacial oxygen coordination and magnetic anisotropy at a ferromagnet/oxide interface [5].

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4:20pm **MI+SA-TuA7 Indirect Modification of Magnetic Surface States by Organic Semiconductor Adsorbates**, ***Daniel Dougherty***, *J. Wang*, North Carolina State University **INVITED**

The spin-dependent electronic coupling of organic molecules to magnetic electrode surfaces is now widely acknowledged to be a crucial factor controlling direct spin injection in organic spintronic devices. This suggests the application of known surface chemisorption principles can guide new developments in this field. However, the kinds of interactions possible at metal-organic semiconductor interfaces are diverse and direct orbital coupling is not always guaranteed even when chemical intuition favors it. In this talk I will report on an unusual observation of indirect orbital coupling at a metal-organic interface even when direct coupling is geometrically plausible. We have observed that adsorption of the organic semiconductor perylene tetracarboxylic acid dianhydride onto Cr(001) decreases the metal *d*-derived surface state lifetime without causing a shift in its energy. This suggests an indirect electronic interaction that contrasts sharply with expectations of *p-d* electronic coupling based on direct chemisorption. Lifetime changes are measured with scanning tunneling spectroscopy as a function of temperature and quantified as arising from a molecule-induced increase in electron-electron scattering rate into bulk bands. Adsorbate-induced effects extend far beyond the adsorption site of the molecule, decaying exponentially away with a characteristic length scale of ~2.4 nm, similar to the carrier mean free path in Cr .

5:00pm **MI+SA-TuA9 Transitioning into the Ga-rich Regime of Ferromagnetic Manganese Gallium Films Grown on Gallium Nitride: Structure and Magnetism**, ***Andrada-Oana Mandru****, *J.P. Corbett, A.L. Richard,* Ohio University, *J.M. Lucy,* Ohio State University, *D.C. Ingram,* Ohio University, *F. Yang,* Ohio State University, *A.R. Smith*, Ohio University

Depositions of magnetic atoms such as Mn onto wide-gap semiconducting GaN surfaces give rise to various MnGa alloyed nanostructures, some having promising magnetic properties. Co-depositions of Mn and Ga result in ferromagnetic alloys that grow with high epitaxial quality on GaN. Such sharp interfaces undoubtedly make MnGa/GaN a very attractive spintronic system. Growth under slightly Mn-rich conditions (Mn:Ga composition ratio ~1.09) causes Mn atoms to incorporate at different rates; surfaces become highly Mn-rich, while the bulk retains a 1:1 stoichiometry. In addition, their magnetic properties could potentially be tailored by altering elemental composition and/or film thickness. Motivated by these intriguing observations and possibilities, we explore what happens when crossing the Mn:Ga 1:1 stoichiometric limit into the less studied Ga-rich side. We combine various techniques to investigate in detail the growth, structure and magnetism of MnGa alloys with different thicknesses and compositions, when coupled with GaN substrates.

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Samples are prepared using molecular beam epitaxy with GaN/Sapphire used as starting substrate. Subsequent depositions involve a fresh film of GaN followed by thin (~30-50 nm) or ultra-thin (~3.3 nm) MnGa films. Manganese and gallium are co-evaporated from Knudsen cells while keeping the substrate temperature at ~250 °C. The growth is monitored in real time using a 20 keV reflection high energy electron diffraction system. *In-situ* room temperature scanning tunneling microscopy investigations reveal highly epitaxial films with smooth surfaces that exhibit a rich variety of reconstructions. The Mn:Ga composition ratios range from ~1 (stoichiometric) to ~0.42 (very Ga-rich), as determined by Rutherford backscattering spectrometry. For stoichiometric films, x-ray diffraction characterizations show primarily MnGa peaks; upon transitioning into the Ga-rich regime, we find a co-existence of Mn_3Ga_5 and Mn_2Ga_5 phases, with Mn_2Ga_5 becoming predominant for the highly Ga-rich samples. Magnetic investigations reveal that all films exhibit ferromagnetism, including the very Ga-rich ones. Vibrating sample magnetometry measurements performed on the thin samples show stepped hysteresis loops, along with a decrease in coercivity and magnetic moment values as the Ga concentration increases. Additional superconducting quantum interference device measurements performed on the ultra-thin samples show that large magnetic anisotropies are induced by decreasing the thickness of our films. Most recently, similar investigations applied to FeGa magnetostrictive alloys reveal very interesting surfaces and magnetic properties.

5:20pm **MI+SA-TuA10 A Depth-Dependent Model for Atomic Valence in Magnetoelectric Systems**, ***Mikel Holcomb***, *R. Trappen, J. Zhou,* West Virginia University*, Y-H. Chu,* National Chiao Tung University*, S. Dong*, Southeast University

Interfacial magnetoelectricity across a multilayer system is known to sometimes result in much larger coupling between electric and magnetism than in single phase systems. The cause has been controversial, but the atomic valence of the magnetic element in these systems is known to change with an applied voltage. We wanted to understand how the interfacial atomic valence was effected as a function of film thickness in thin films of $La_{0.7}Sr_{0.3}MnO_3$ on $PbZr_{0.2}Ti_{0.8}O_3$. To separate the Mn valence at the interfacial layer with PZT from the bulk region of LSMO, we took advantage of the drastically different attenuation length of two techniques: x-ray absorption in *L*-edge total electron yield mode and *K*-edge fluorescence yield mode. By globally fitting both sets of experimental results, we were able to develop a depth-dependent model to estimate the layer by layer valences in our materials as a function of thickness. This empirical model was developed under the guidance of theoretical work from a two-orbital double exchange model, which also explored the effects of substrate termination and ferroelectric polarization direction. Estimates based on the data and models for surface, interface and bulk valence as well as surface and interface length scales will be discussed.

5:40pm **MI+SA-TuA11 Atomic-Scale Magnetism on a Complex Insulating Surface**, ***Barbara Jones***, IBM Research - Almaden*, O.R. Albertini,* Georgetown University*, S. Gangopadhyay,* IBM Research - Almaden*, A.Y. Liu*, Georgetown University

We will describe and analyze the unusual magnetic properties of transition metal atoms on complex, hybrid surfaces. In collaboration with IBM Almaden's Scanning Tunneling Microscopy team, we use DFT+U to calculate the properties of transition metal atoms on one or two atomic layers of insulator on top of a metal such as silver. We show the transition of the interface from bulk insulator or metal to a nanolayer that is nominally insulating, but that hybridizes strongly with the addition of a magnetic adatom to produce a long spin-polarized tail into the vacuum, akin to a metal. We report the results of detailed calculations of a range of magnetic atoms (Mn, Fe, Co, Ni) on MgO/Ag. MgO is a common spintronic insulator, but in a nanolayer on metallic Ag, its behavior is not that of the bulk. We find that each magnetic atom has its own surface signature, with very different local spin and charge interactions with this surface, and compare it to that of other related systems. Using an onsite Hubbard U parameter which we determine from first principles, we are able to study the variability of the magnetic moment and nature of bonding. The magnetic adatoms affect the surrounding interface layer in unexpected ways. We are able to obtain interesting insights which help us understand how magnetism propagates along surfaces as well as between interfaces. These systems have potential for future spintronics or quantum computing applications.

6:00pm **MI+SA-TuA12 Substrate Induced Spin-state Locking of $[Fe(H_2B(pz)_2)_2(bipy)]$ on Au(111)**, ***Sumit Beniwal****, *X. Zhang, S. Mu,* University of Nebraska - Lincoln*, A. Naim, P. Rosa, G. Chastanet,* CNRS Universite de Bordeaux, France*, J. Liu,* Northeastern University*, G. Sterbinsky, D. Arena,* Brookhaven National Laboratory*, P.A. Dowben, A. Enders*, University of Nebraska - Lincoln

Spin-crossover (SCO) complexes hold promise for spintronics applications as room-temperature single molecular magnets. Their signature functionality arises from a central transition metal atom, which is in a d^4-d^7 configuration in a (pseudo)octahedral N_6 environment and can be switched between a diamagnetic low-spin (S=0) and a paramagnetic high-spin (S=2) state by external stimuli such as temperature, pressure, light and electric field. The switching of the molecular spin-state is accompanied by change of other physical and electronic properties of these complexes, such as color, magnetic susceptibility and electrical conductivity. Application in devices requires that the molecules are in contact with metal electrodes, which can significantly alter their electronic and magnetic properties. This study makes use of a comprehensive suite of surface-sensitive spectroscopy and microscopy tools to investigate the electronic properties of SCO complex $[Fe(H_2B(pz)_2)_2(bipy)]$ on Au(111) to identify characteristic signatures of spin-state of the molecules across thermal spin transition temperature. Variable temperature scanning tunneling microscopy, performed as a function of film thickness, revealed that ordering in the molecular layers is established as the films are cooled well below their spin transition temperature, and this ordering is maintained when the films are brought back to room temperature. Temperature and thickness dependent studies of electronic structure using X-ray photoemission (XPS), X-ray absorption spectroscopy (XAS) and inverse photoemission (IPES) on surface supported networks, reveal substrate effects on the spin state. Satellite features in core level XPS Fe $2p_{3/2}$ peaks are characteristic of the spin transition, whereas angle-resolved XPS (ARXPS) helps to separately determine the electronic structure of interfacial molecules and of molecules away from the interface. Fe L-edge X-ray absorption XAS spectra taken on ultrathin films suggest that the substrate inhibits thermally induced transitions of the molecular spin state, so that both high-spin and low-spin states are preserved far beyond the spin transition temperature of free molecules. These results demonstrate that thin films of the spin crossover complexes studied have distinctively different phase transition behavior as compared to bulk-like samples, which is evidence that interface interactions can considerably affect the molecules' structural conformation, spin state as well as electronic properties. Understanding such interface effects can help establish conditions to control the spin state of molecules and to engineer spin state transitions.

MEMS and NEMS
Room: 211A - Session MN+BI-TuA

BioMEMS/NEMS, Wearable and Implantable Devices
Moderator: Wayne Hiebert, University of Alberta and The National Institute for Nanotechnology, Beth L. Pruitt, Stanford University

2:20pm **MN+BI-TuA1 Entrepreneurial Environment for Implantable and Wearable BioMEMS**, ***Kurt Petersen***, Silicon Valley Band of Angels **INVITED**

Several converging trends are transforming the entrepreneurial process for starting MEMS companies and for transitioning MEMS devices into production and into the market. First, it is well-known that recent market set-backs have caused traditional VC funds to view any hardware start-ups with renewed scrutiny and skepticism. Hardware, and particularly bioMEMS, start-ups typically require large amounts of capital ($50-$100M) and many years (7-10), before getting close to a reasonable exit. This large investment in money and time is on top of the already inherently risky prospects for such a start-up being commercially successful. Secondly, MEMS is recognized, by investors, by foundries, and by large consumer electronics companies, as a very successful new product area because of the huge up-take of MEMS components in mobile devices during recent years. Third, key strategic issues in huge upcoming new consumer markets, such as wearables and IoT, are sensors and contextual awareness; areas which are uniquely solved by MEMS devices. And fourth, the sheer number of successful, high volume MEMS devices currently on the market, has created a huge pool of skilled MEMS developers and manufacturers which can be drawn upon for new devices and new start-up companies. All these factors dramatically influence how such companies get funding and how

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they operate. We will discuss all these issues as they relate specifically to new implantable and wearable MEMS start-up companies. As examples, we will also discuss a number of current technical developments/devices/companies involving implantable and wearable bioMEMS.

3:00pm **MN+BI-TuA3 MEMS Sensors Make Up the Frontline of Wireless Health Solutions: Tremendous Growth Prospects**, ***Mehran Mehregany***, Case Western Reserve University **INVITED**

Use of sensor-enabled wearable wireless health solutions to monitor the health condition of chronic disease patients is key to the quality of life of the patient and to reduction of cost of health care—by keeping the patient out of the hospital and emergency rooms. Monitoring for early intervention is key to avoiding long-term adverse outcomes for those at risk of developing chronic diseases. This presentation will elaborate on the important role that MEMS sensors play in enabling wearable, health monitoring solutions. Capturing data is the key to such solutions, which requires sensors of various modalities. MEMS sensors have the advantage s of miniaturization, integration and batch fabrication—driving size, performance and cost advantages.

Annual heath care expenditure in the United States was ~$2.7 trillion in 2011 (i.e., $8,680 per person), well above other developed countries. Health spending grew 3.9% in 2011, the same as in 2009 and 2010; spending as a share of GDP has remained stable from 2009 through 2011, at 17.9%. The US health care system is built on fee-for-service, wherein the service is reactive to illness. An aging population, longer lives and increasing cases of chronic diseases are some of the key drivers escalating health care expenditures.

Chronic diseases account for 75%+ of the US health care expenditures, i.e., $2 trillion. 141 million (45% of the population) have at least one chronic disease, 72 million of which have two or more. Top 10 significant chronic diseases are: hypertension, obesity, arthritis, asthma, chronic kidney disease, depression, chronic obstructive pulmonary disease (COPD), diabetes, sleep disorder and heart failure.

4:20pm **MN+BI-TuA7 GC-MS to GC-NOMS: A Step Towards Portable Analysis**, ***Anandram Venkatasubramanian***, *S.K. Roy, V.T.K. Sauer, W.K. Hiebert*, National Institute for Nanotechnology and University of Alberta, Canada

The Gas Chromatography (GC) – Mass Spectrometer (MS) system is the industry benchmark in research and chemical analysis. However given that MS systems are large and complicated instrumentation, chemical analyses have a long turnaround time. In this regard, portable GCs have carved a market niche but they have poor sensitivities. Recent demonstrations with Nanooptomechanical (NOMS) resonators at atmospheric pressure have proven that these kind of sensors have the breakthrough potential to improve the sensitivity of portable GCs. In this regard we have built an experimental rig to integrate the GC system with our NOMS device. The goal of this study is two-fold. One will be to replace the GC sensor with NOMS devices, integrate with the portable GCs for better sensitivity, and ultimately match the analytical power of conventional GC-MS. The other will be to demonstrate the NOMS sensing capabilities for next generation genomic applications like personalized medicine. In this regard, we have designed and developed a free space interferometry system. The probe laser is coupled in and out of the photonic waveguide using grating couplers. Using the evanescent field of the waveguide, the shift in resonant frequency of the nanoscale resonators is recorded using lock in amplifier. Here we have tracked the response of both the ring resonators using the photodetector output and the nanomechanical resonator using the phase locked loop (PLL). GC peak sensing can be done with either or both of the mechanical and the photonic sensors. During the initial testing with analyte standards we observed the ring resonator to respond faster than the nanomechanical resonator on par with the GCs flame ionization (FID) detector. We were also able to capture the analyte peaks effectively with the sensitivity of the resonators to be about 77 zg/Hz.

4:40pm **MN+BI-TuA8 Label-Free Biosensing Platform Integrating a Nanofluidic Preconcentrator with Surface Plasmon Resonance Sensors**, ***Wei-Hang Lee***, *P.S. Chung,* National Taiwan University, Taiwan, Republic of China, *P.K. Wei,* Academia Sinica, Taiwan, Republic of China, *W.C. Tian*, National Taiwan University, Taiwan, Republic of China

For bioMEMS applications, the integration of preconcentration and sensing has been studying to detect low-abundance analytes without labelling. In the past few years, an electrokinetic trapping (EKT)-based nanofluidic preconcentrator had been reported for providing a million-fold concentration factors that enable the validation of concentration process and the detection of trace and fluorescence-labelled analytes. However, the use of fluorescence-labelled analytes has suffered several disadvantages, e.g., additional sample preparation, high cost of labeling reagents, and difficulty in analyzing trace analytes. To monitor the concentration process without labelling, previously we have presented a real-time dual-loop electric current measurement system for label-free EKT-based nanofluidic preconcentrators. In this work, we further demonstrate a label-free biosensing platform by integrating a label-free nanofluidic preconcentrator with label-free SPR sensors.

The label-free biosensing platform was realized by a nanofluidic preconcentrator and two nanograting-structured SPR sensors. The preconcentrator is consisted of two parallel microchannels, i.e., one concentration channel and one buffer channel, cast in PDMS and connected by nanochannels. The two SPR sensors, i.e., one for control group and the other for experimental group, are fabricated on glass slide by e-beam lithography, e-gun evaporation and lift-off process. Then, we patterned a Nafion thin film on glass and at the position adjacent to the SPR sensors by using a microflow patterning method. Finally, the PDMS-based microchannels were sealed onto the by oxygen plasma bonding process.

We have demonstrated the ultra-sensitive label-free biosensing platform by detecting the amplified redshift magnitude of a specific range of a SPR spectrum. First, before preconcentration process, several reference spectra were measured. Second, after ten-minute preconcentration process for the 20 ng/ml BSA in PBS, a 5 nm-redshift spectrum was measured. Comparing the experimental spectrum with the reference spectra, the redshift magnitude of 20 ng/ml BSA in PBS after preconcentration process is equivalent to that of the 200 μg/ml BSA in PBS. Hence, we demonstrate a preconcentration factor of ten-thousand folds and a sensing limit of at least 20 ng/ml BSA in PBS in this label-free biosensing platform.

In summary, by utilizing the electric current measurement system and the commercial optical system, low abundance analytes can be preconcentrated and sensed by the developed biosensing platform, which enables a label-free approach on preconcentrating and detecting trace molecules with high sensitivity.

5:00pm **MN+BI-TuA9 Microparticle Patterning Using Multimode Silicon Carbide Micromechanical Resonators**, ***Hao Jia***, *H. Tang, P.X.-L. Feng*, Case Western Reserve University

In recent years, there have been increasing interests in manipulating and patterning microparticles and biological cells on microscale planar surfaces[1],[2],[3], among which "Chladni figures"[4], enabled by resonant microelectromechanical systems (MEMS)[5], offer a noninvasive, fast, and highly-controllable approach by simply programming frequency.

In this work, we report experimental demonstration of manipulating microparticles in fluidic environment using multimode silicon carbide (SiC) MEMS resonators, forming diverse microscale Chladni patterns. Silica microspheres with various diameters (0.96, 1.70, 3.62, 7.75μm) sprinkled onto suspended surfaces of SiC doubly-clamped beams (60×10μm, 100×10μm and 100×20μm) and square trampolines (50×50μm and 90×90μm) are quickly manipulated into one dimensional (1D) and two dimensional (2D) geometrical patterns, such as "dots (.)", "line (/)", "cross (×)" and "circle (○)" by piezoelectrically exciting those resonators at their flexural resonance modes.

SiC MEMS resonators, with its unique biocompatibility[6](indicating biological applications), are fabricated based on a SiC-on-Si platform, with device structures patterned by the focused ion beam (FIB) and suspended by an isotropic Si etching (HNA, 10% HF: 70% HNO_3=1:1). Multimode resonances in liquid (up to 5MHz) are characterized using laser interferometry[6], based on which the piezoelectric driving frequencies are switched in real-time to strongly excite the microspheres and manipulate them into a series of Chladni patterns. Such SiC resonating platform, by taking advantage of its straightforward device fabrication and engineerable multimodes, offer new means for microparticle manipulation and patterning, and may further facilitate cell manipulation, and other biophysical and biomedical studies.

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Manufacturing Science and Technology
Room: 114 - Session MS-TuA

Working with National Labs and User Facilities
Moderator: Charles Eddy, Jr., U.S. Naval Research Laboratory, Bridget Rogers, Vanderbilt University

2:40pm **MS-TuA2 Research Opportunities at the Cornell Nanoscale Science and Technology Facility, a member of the National Nanotechnology Coordinated Infrastructure.**, ***Michael Skvarla**, D. Ralph*, Cornell NanoScale Science and Technology Facility

The Cornell Nanoscale Science and Technology Facility (CNF) is one of a network of open-access shared facilities partially subsidized by the US National Science Foundation to provide researchers with rapid, affordable, shared access to advanced nanofabrication tools and associated expertise. Projects can be accomplished either hands-on or remotely. Hundreds of engineers and scientists nationwide, from academia, industry, and government, utilize CNF to make structures and systems from the nanometer to the centimeter scale. CNF offers unique capabilities in world-leading electron-beam lithography, advanced stepper photolithography, soft lithography, and rapid prototype development, along with the ability to deposit, grow, and etch a very wide variety of materials. CNF's technical staff are dedicated full-time to user support, providing one-on-one help with process development, training, and troubleshooting. They can offer expertise for a wide range of fabrication projects, including not just electronics but also nanophotonics, magnetics, MEMS, thermal and energy systems, electrochemical devices, fluidics, and the life sciences. More than 30% of CNF's users come from biology/bioengineering fields. All users are welcome; no experience in nanofabrication is necessary and a central part of CNF's mission is to assist users from "non-traditional" fields seeking nanofabrication techniques for the first time. CNF's user program is designed to provide the most rapid possible access (typically 2 weeks from first contact) with the lowest possible barriers to entry (users retain full control of their IP, with no entanglement by CNF or Cornell University). More than 85% of CNF's external academic users come from institutions with their own local cleanroom facilities, but still they utilize CNF for advanced capabilities, staff expertise, or tool reliability not available locally.

This talk will explore the tools, services and advice available to CNF users, and show examples of ongoing work. We will also provide the latest details on the National Nanotechnology Coordinated Infrastructure (NNCI) program, a new NSF-sponsored network of shared facilities similar to CNF that is in the process of being organized at abstract submission.

We invite you to explore the CNF and NNCI and discuss ways we can help bring your research visions to fruition. CNF's User Program Managers will at no cost provide detailed processing advice and cost estimates for potential new projects. The CNF technical staff also meets every Wednesday afternoon for conference calls where we welcome questions about any topic related to nanofabrication. Visit cnf.cornell.edu to contact us and get started.

3:00pm **MS-TuA3 The CNST NanoFab at NIST is Open for Business**, ***Vincent Luciani***, NIST Center for Nanoscale Science and Technology

The NIST Center for Nanoscale Science and Technology (CNST) supports the U.S. nanotechnology enterprise from discovery to production. As part of the CNST, the shared-use NanoFab provides its users rapid access to a comprehensive suite of tools and processes for nanoscale fabrication and measurement. The CNST NanoFab at NIST is part of the Department of Commerce and therefore puts a high priority on operating a business friendly, easily accessible facility. The same rates are applied to all users, whether from industry, academia or a CNST colleague down the hall. Applications are accepted at any time and are reviewed and processed every week. Also, NIST does not claim any inherent rights to inventions made in the course of a NanoFab project. The NanoFab features a large, dedicated facility, with tools operated within a class 100, 8,000 square foot (750 m^2) cleanroom or in adjacent laboratories that have superior air quality along with temperature humidity, and vibration control. Over 80 major process tools are available, including but not limited to e-beam lithography, 5x reduction stepper photolithography, nano-imprint lithography, laser writing for mask generation, scanning and transmission electron microscopy, metal deposition, plasma etching, chemical vapor deposition, atomic layer deposition, deep silicon etching and ion beam etching. The NanoFab staff consists of scientists, engineers and technicians that specialize in all areas of nanofabrication and provide training and ongoing technical assistance to users. Our goal is to be a catalyst to our user's success and to help nurture nanotechnology commerce in the Unites States. Project applications and instructions are easily available on the web. Users inside NIST and from all around the country are provided on-line access to tool schedules and the tool reservation system. From physicists, engineers and biologists to medical researchers, users find common ground at the nanoscale in the CNST NanoFab.

3:20pm **MS-TuA4 The Molecular Foundry: A Knowledge-Based User Facility for Nanoscale Science**, ***Branden Brough***, The Molecular Foundry, Berkeley Lab

The Molecular Foundry, a nanoscience research center at Lawrence Berkeley National Laboratory provides communities of users with access to expert staff and leading-edge instrumentation to enable research on the nanoscale in a multidisciplinary, collaborative environment. Selected through an external peer-reviewed proposal process, users come from academic, industrial or national laboratories, both domestic and international, free of charge. Located in the Bay Area's active academic environment and near Silicon Valley, research is organized into seven closely coupled facilities: Inorganic, Organic, and Biological facilities for synthesis, preparation, and assembly; Nanofabrication, for processing and integration; the National Center for Electron Microscopy and Imaging and Manipulation, for characterization; and Theory, for understanding and predicting material properties. In summarizing the Foundry program, a selection of recent results will be highlighted such as those using automated high-throughput synthesis of nanocrystals, 2d materials, metal-organic frameworks, and sequence-specific polymers; aberration-corrected electron microscopy and electron tomography of individual proteins; 20 nm resolution optical spectroscopy; synthesis and simulations of nano-hybrid thermoelectrics and electrode-electrolyte interfaces; and interfaces between inorganic nanoscale building blocks with living cells.

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

4:40pm **MS-TuA8 User Opportunities at the Center for Nanoscale Materials: From Hybrid Nanomaterials to Tailoring Nanoscale Interactions**, ***Kathleen Carrado Gregar***, Center for Nanoscale Materials at Argonne National Laboratory

The mission of the Center for Nanoscale Materials (CNM) user facility at Argonne National Laboratory is to provide expertise, instrumentation, and infrastructure for interdisciplinary nanoscience and nanotechnology research by scientists and engineers from academia, industry, and government agencies. The Center's goal is to support and explore ways to create functional hybrid nanomaterials and to tailor nanoscale interactions for energy-related research and development programs. The CNM addresses grand challenges in energy and information conversion and transport, while furthering the Department of Energy (DOE) missions in energy generation, storage, and efficiency. Unique capabilities at CNM include a large clean room, expansive synthesis and nanofabrication resources, a hard x-ray nanoprobe at the Advanced Photon Source synchrotron, myriad scanning probes including low temperature, ultrahigh vacuum STMs, TEMs with in situ holders and chromatic aberration-correction, a 30 TFlop supercomputer, oxide MBE, and ultrafast optical probes. Another CNM asset includes outstanding staff with expertise in nanocrystal and nanoparticle synthesis, complex metal oxides, nanophotonics, plasmonics, scanning probe microscopy, nanofabrication, functional bio-inorganic hybrid nanomaterials, and theory, simulation and modeling. Core technological materials range from photocatalysts to graphene to nanocrystalline diamond. All of these capabilities and expertise are available to the international research community through peer-reviewed user proposals; access is free of charge for allocated non-proprietary research in the public domain. CNM is one of DOE's premier Nanoscale Science Research Centers serving as the basis for a national program encompassing new science, new tools, and new computing capabilities for research at the nanoscale (https://nsrcportal.sandia.gov). Recent staff and user research highlights will be presented, painting a picture of present and future nanoscience and nanotechnology at the CNM (www.anl.gov/cnm).

The Center for Nanoscale Materials, an Office of Science user facility, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract no. DE-AC-02-06CH11357.

5:00pm **MS-TuA9 Using EMSL Capabilities to Advance Your Research**, ***Donald Baer**, M. Engelhard*, Pacific Northwest National Laboratory

EMSL, the Environmental Molecular Sciences Laboratory, is a Department of Energy user facility. EMSL's vision is to pioneer discoveries and effectively mobilize the scientific community to provide the molecular science foundation for the DOE Office of Biological and Environmental Research research priorities and our nation's critical biological, environmental and energy challenges. To accomplish this vision, EMSL science is focused in four areas: biosystem dynamics and design, atmospheric aerosol systems, terrestrial and subsurface ecosystems and energy materials and processes. Processes that occur at surfaces and interfaces are critical in each of these areas and EMSL provides a wide range of unique and state-of-the-art spectroscopy, microscopy, magnetic resonance and computational capabilities to advance the relevant sciences (www.emsl.pnnl.gov).

Scientific discovery and technological innovation in environmental molecular sciences are facilitate by EMSL's integrated set of experimental and computational resources. Researchers are invited to apply for the opportunity to collaborate with recognized experts and use state-of-the-art instruments and facilities. Researchers use resources at EMSL for little or not cost if results are shared in open literature. The primary mode for obtaining access to EMSL is through an annual call for proposals oriented around specific topics identified with each science theme. This call appears in late December, Four-page proposals are due in March. As a multi-capability facility, we seek proposal that combine scientific innovation through instrument integration combining computational and experimental approaches for discovery. Increasingly we are developing and using capabilities that enable real-time *in situ* measurements in a variety of environments.

5:20pm **MS-TuA10 From Neutron Nanoscience to Direct-write Nanofabrication at the Center for Nanophase Materials Sciences**, ***Olga Ovchinnikova***, Oak Ridge National Laboratory

The Center for Nanophase Materials Sciences (CNMS) at Oak Ridge National Laboratory (ORNL) is a multidisciplinary user facility that provides the research community with access to expertise and equipment to address the most challenging issues in nanoscience. Industrial, government and academic researchers from around the world may access capabilities in functional imaging, atom-precise synthesis, and nanofabrication. The CNMS is a leader in a range of advanced nanofabrication techniques including electron beam assisted deposition on the sub-10 nm level using both gas and liquid precursors as feedstock material, 3D fabrication and atomically precise material sculpting, as well as direct matter manipulation on the atomic level by electron beams to induce material functionality. Spatially resolved quantitative measurements of physical and chemical properties of materials are available to users through unique measurement capabilities of band excitation scanning probe microscopy, scanning transmission electron microscopy, helium ion microscopy, and atom probe tomography. Furthermore, theoretical and computational approaches are available to CNMS users, as frameworks for deep-data analytics methods for imaging, and computational prediction of functional and physical properties in nanostructures, benefiting from the broad ORNL computational capabilities. Located adjacent to the Spallation Neutron Source at ORNL, CNMS acts as a gateway for the nanoscience community to ORNL's world-class neutron science facilities, by providing diverse complementary capabilities such as selective deuteration, sample environments for multi-modal measurements, fabrication of templates for neutron reflectivity experiments, and many other materials science capabilities to complement neutron results. As one of the five Department of Energy Nanoscale Science Research Centers (see nsrcportal.sandia.gov), CNMS makes all of these capabilities, and the staff expertise to fully benefit from them, available free of charge to users who intend to publish the results, or at-cost for proprietary research, as described at cnms.ornl.gov. [The CNMS at Oak Ridge National Laboratory is a DOE Office of Science User Facility.]

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.

References:

[1] C. Martella, D. Chiappe, P. Delli Veneri, L.V. Mercaldo, I. Usatii, F.Buatier de Mongeot, Nanotechnology 24 (22), 225201 (2013).

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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.

Plasma Science and Technology
Room: 210A - Session PS1-TuA

Novel Materials and Etch Chemistry
Moderator: David Lishan, Plasma-Therm LLC

2:20pm **PS1-TuA1 Low-Damage Etching Technology for Nitride Semiconductor Devices**, ***Makoto Sekine***, *Z. Liu, J. Pan, K. Ishikawa, K. Takeda, H. Kondo, M. Hori*, Nagoya University, Japan **INVITED**

Plasma etching of GaN is necessary for fabricating high performance Nitride semiconductor devices. However plasma exposure causes defects and residues, which could reduce the performances. It is required that the plasma induced damages (PID) should be removed especially in the power electronics device fabrication. Post annealing could recover PID, but preferential N loss causes Ga-rich surface. The stoichiometric surface was reported to be deteriorated with annealing up to 1000°C after N_2^+ sputtering at room temperature (RT)[1], We have revisited the surface reactions at high temperature (HT). We made a HT etcher. A VHF-ICP was generated and 13.56-MHz rf power was applied to the substrate. Sample stage can be heated up to 800°C by an IR lamp as fast as 100°C/s.

GaN surface was roughened with 9.88 nm RMS as exposed to Ar plasma at 600°C. XPS showed Ga metallic state or Ga cluster with the shoulder peak at 18.9 eV in Ga 3d. In contrast, no significant roughness increase (1.46 nm) was observed after N_2 plasma at 600°C. Nevertheless, the HT N2 plasma failed to provide a preferable PL property[2].

For Cl_2 plasma, PL spectra of GaN etched at HT showed no obvious variation of yellow luminescence at 2.2-2.3 eV, suggested no Ga vacancies were formed. We focused on the near band edge emission (NBE) at 3.4 eV. The PID in bulk GaN behave as nonradiative centers of deep level states, which trap and recombine carriers. The NBE intensities for all GaN films etched at HT were degraded and as a consequence, the etching process at 400°C was optimum, because of its preferable stoichiometry, PL and smooth surface.

By covering the sample surface with a transparent window with or without the gap, we separated the effects of ion, photon and radical exposures. It was found the ion-induced damages dominated at 300°C, then decreased at 400°C, and removed at 500°C. Furthermore, photon-induced damages were not observed up to 400°C. Above 500°C, PL properties were degraded by photon. Since photons could not mainly induce damages at RT[4], the synergy with thermal annealing enhanced the PL deterioration.

Therefore, by the results of depressed ion-induced damages and undeveloped photon-induced damages with a smooth surface at 400°C, the Cl_2 plasma etching at 400°C is most appropriate to the low-damage process for GaN-based devices.

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3:00pm **PS1-TuA3 Limitation of Surface Defects in GaN Deep Etching**, *N. Gosset*, ***Thomas Tillocher***, GREMI CNRS/Université d'Orléans, France, *J. Ladroue*, ST Microelectronics, France, *P. Lefaucheux*, GREMI CNRS/Université d'Orléans, France, *M. Boufnichel*, ST Microelectronics, France, *R. Dussart*, GREMI CNRS/Université d'Orléans, France

Gallium nitride (GaN) is a III-V semiconductor with attractive physical properties for power microelectronics. It actually combines a wide and direct bandgap, a high electron mobility and strong chemical bonds. Therefore, GaN power components can operate under higher temperature, higher power and higher frequency than silicon devices.

For Schottky diodes with pseudo-vertical structure, GaN MESA features with a height between 6 and 10 µm are required. This is considered as deep etching, compared to the thickness typically etched for light emitter devices (a few hundred nm). Ion-enhanced plasma etching with chlorine-based chemistry is commonly used for GaN deep etching.

Previous studies have already shown that GaN can be etched in Cl_2/Ar inductively coupled plasmas (ICP) with etch rates as high as 1 $\mu m.min^{-1}$. However, after etching, the etched surface exhibits three types of defects such as columns, pits and a high roughness (“White GaN”). Columns and pits are related to nanopipes and dislocations created during epitaxial growth of GaN. In addition, oxygen based species, coming from either the SiO_2 coverplate and mask, or the alumina/quartz tube, play an important role in the columnar regime. They preferentially oxidize dislocations, leading to the observed columns. “White GaN” origin is a surface over-oxidation. Such defects must be suppressed in order to provide good electrical contact.

A comparative study of GaN etching has been performed on different reactors: an ICP reactor with a diffusion chamber, another ICP reactor with no diffusion chamber, a dual-frequency capacitive reactor and an Ion Beam Etching system. The etched surface state was subsequently analyzed by means of SEM, EDX, AFM and XPS. This study revealed a correlation between the etch rate, the surface defects density and the surface composition. Actually, with the IBE chamber, the etch rate was the lowest and no defects were observed on the surface. The dual-frequency capacitive reactor allows the highest etch rate and no defects were found on the surface. But, the Ga:N relative density was altered in both cases, resulting in poor electrical properties. Consequently, a trade-off should be made between process performances and electrical properties. ICP chambers met this compromise.

Moreover, it has been demonstrated that surface fluorination, by addition of a fluorine-containing gas, leads to a limitation of surface defects. Fluorine species are able to protect GaN surface with the formation of a Ga_xF_y -like "passivation layer", detected by XPS. This result led to the development of a defect-free time-multiplexed etching process consisting in alternating etching and passivation steps.

3:20pm **PS1-TuA4** ***In Situ* Monitoring of GaN in Process Plasma**, ***Daisuke Ogawa***, *Y. Nakano, K. Nakamura*, Chubu University, Japan

Next to a great success of blue LEDs, gallium nitride (GaN) is now looking for another success, the application with high-power devices. The wide bandgap of GaN is attractive when considering the integration and fabrication of devices on a substrate. The integration process requires the use of plasma, but the plasma sometimes creates undesirable change on devices, noticed as plasma-induced damages (PID). Therefore, it is important to understand how process plasma creates changes on GaN and what mainly causes the change.

In-situ monitoring is one of ways to understand the damage development of GaN. Towards to the goal, we have used steady-state photoluminescence (PL) emitted from the surface of GaN. The PL represents the optically-transferrable intermediate states that are mainly created with the defects and impurity in GaN. The depth of the PL measurement depends on the wavelength of excitation. Our experiment setup uses 313 nm wavelength for the excitation so that we basically monitored the change of the intermediate states down to ~75 nm below the top surface.

Our in-situ measurements showed that the exposure of argon plasma changed PL spectrum from the GaN; the total PL intensity turned down to 33 % of the original spectrum. We also increased the chuck bias, showing that the total PL intensity decreased even worse. This means that the argon ion affected the change of PL in our system assuming that plasma density stayed the same. We also made ex-situ measurements with X-ray photoelectron spectroscopy (XPS). The measurement showed that the change of atomic distribution was observed down to 4 nm at deepest. In this depth range, gallium and nitrogen atoms dissociated from the surface, and oxygen atoms defused into deeper levels. However, this depth was only ~5 percent of the depth where PL spectrum informs us. This means that the change of PL was caused by the structural change in GaN, such as crystal dislocation.

We also changed the gas that formed the plasma. In general, chlorine gas is utilized to etch GaN. In this measurement, we used the mixture gas of argon and chlorine with the ratio of 2:1. Interestingly, the PL from GaN stayed almost constant even when GaN was exposed into the plasma. We double-checked the etch rate, finding the rate at 100s nm/min. This result indicates that chlorine likely etched GaN without making a major change in the optical intermediate states even though argon could have made some damages during the plasma exposure.

In this presentation, we will show our latest analysis of damage development of GaN that is exposed in plasma, in particular, the plasma that is possibly used in the material process.

4:20pm **PS1-TuA7 Thermodynamic-aided Selection of Non-PFC Plasma Chemistries**, ***Nicholas Altieri***, *J.K.C. Chen, L. Minardi, J.P. Chang*, University of California Los Angeles

Continued reduction in the size of microelectronics and nanoscale features has necessitated the use of low-k dielectric interlayer materials in an effort to curtail parasitic capacitance and RC delay. Patterning these low-k films requires consideration of both etching efficacy and environmental impact. To address these issues, a generalized methodology is developed based on a thermodynamic approach to analyze etchants and additive gases to assist in selection of plasma chemistries whose environmental effects can be more easily mitigated.

Thermodynamics is an enabling tool for assessing a reacting system, such as plasma etching of carbon doped porous silica, specifically through analysis of Gibbs free energy. A system at equilibrium has reached a minimal Gibbs free energy which can be expressed as the sum of its constituents and their corresponding chemical potentials. With known reactants, potential products, and free energies of formation as inputs, the total Gibbs energy is minimized to calculate an output quantity of each species. This calculation was then repeated across a range of temperatures at fixed pressure. Using CF_4 etching of silica as the reference and monitoring the formation of volatile etch product $SiF_4(g)$ via volatility diagrams, a range of carbon doped porous silica, a list of viable etchants including perfluorocarbon gases, $NF_3(g)$, $CF_3I(g)$, as well as additive gases such as $H_2(g)$ and $NH_3(g)$ are examined. Based on thermodynamic calculations, $NF_3(g)$, a non-PFC gas with high abatement efficiency was predicted to generate the highest pressure of $SiF_4(g)$ overall. $CF_3I(g)$, though calculated to be not as effective as $NF_3(g)$, is another alternative due to its short atmospheric lifetime and low global warming potential. On the other hand, $H_2(g)$ was found to be the most effective additive with fluorocarbon etchants. $CF_4(g)$ and $CHF_3(g)$ were studied separately with varying hydrogen addition to validate the thermodynamic calculations. Optical emission spectroscopy was used in parallel to monitor atomic fluorine intensities at 685.6 and 703.7 nm as a function of $H_2(g)$ feed percentage. Discharges of $CF_4(g)$ mixed with 20% $H_2(g)$ and CHF_3 with 10% $H_2(g)$ resulted in maximal etch rates of 215 nm/min and 166 nm/min respectively. A trend similar to etch rate dependence on feed composition was seen in the spectra of atomic fluorine, with maximal intensities recorded for CF_4 and CHF_3 at 20% and 10% H_2, respectively.

4:40pm **PS1-TuA8 Enhancing Selectivity for Self-Aligned Contact Etching by Employing Dual Fluorocarbon Etch Gas Processes**, ***Jeffrey Shearer***, IBM Research Division, *S.U. Engelmann, R.L. Bruce, E.M. Sikorski,* IBM Research Division, T.J. Watson Research Center, *T. Suzuki, M. Nakamura, A. Ito,* ZEON Chemicals L.P., *G. Matsuura, H. Matsumoto,* Zeon Corporation, Japan, *B. Messer, K. Horvath, A. Metz,* TEL Technology Center, America, LLC, *J.C. Arnold,* IBM Research Division, *E.A. Joseph*, IBM Research Division, T.J. Watson Research Center

As the industry moves from 10nm node to 7nm node and beyond, self-aligned contact (SAC) etch is becoming one of the most critical and challenging process elements in logic chip manufacturing. Extremely high selectivites are required to adequately stop on spacer and hard mask materials in addition to the ever continuing trend of scaling critical dimensions (CDs). For the self-aligned contact etch this translates into a classic trade-off relationship between increased selectivity by fluorocarbon deposition and random etch stop due to ion/neutral flux imbalances at reduced dimensions.

Our team has recently introduced a new etch gas (C_5HF_7) which is able to etch by selective deposition of a fluorocarbon (FC) layer, where the elemental fluorine content was reduced due to feedgas optimization. Even though the C_5HF_7 gas yielded better protection of the spacer material than the comparable C_4F_6 process, adequate etch depth was not achieved in aggressive 10nm test structures (etch stop was observed).

We enhanced this process further by decomposing the etchant supply of the fluorocarbon gas by the use of dual FC etch chemistries. While one FC gas is targeted to deliver radicals for FC deposition and selectivity enhancement, another FC gas is added to supply FC radicals that promote the oxide etch. We are reporting our results from this approach by two trusts: On a more fundamental level, we evaluated the dual FC etch gas approach in detail, with gas optimization and a survey of multiple spacer materials. We found that for SiN spacer materials our C4F6 process showed selectivities of approx. 9, the C_5HF_7 process showed selectivities of up to 23 and the dual FC process showed selectivities of up to 38.

Furthermore, C_5HF_7 has been deployed for SAC applications in 10nm and 7nm product demonstrations. This paper will show that this new gas is able to match the performance of the C_4F_6 while at the same time significantly improving raw process time.

This work was performed by the Research Alliance Teams at various IBM Research and Development Facilities.

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5:00pm **PS1-TuA9 Pushing the Limits of Dielectric Etch with Novel Fluorocarbon Etch Gases**, ***Robert Bruce***, IBM Research Division, T.J. Watson Research Center, *T. Suzuki,* ZEON Chemicals L.P., *J. Lee,* IBM Albany Nanotech Center, *E.A. Joseph, S.U. Engelmann,* IBM Research Division, T.J. Watson Research Center, *A. Itou, M. Nakamura,* ZEON Chemicals L.P., *G. Matsuura,* Zeon Corporation, Kawasaki, Japan, *J.C. Arnold,* IBM Albany Nanotech Center, *E.M. Sikorski*, IBM Research Division, T.J. Watson Research Center

As the semiconductor industry continues to drive critical dimensions smaller moving to 7nm technology node and beyond, the challenges to dielectric etch for BEOL fabrication become ever greater. Plasma etch using fluorocarbon passivation gas to establish selectivity and maintain straight profiles during pattern transfer has been the mainstay of patterning into dielectrics. We have previously reported the superior performance of etching SiO2 and low-k using the hydrofluorocarbon gas C5HF7, which had greater selectivities and reduced sidewall damage compared to other passivation gases such as C4F8 and C4F6. This was due to the greater deposition behavior of C5HF7 because of fluorine scavenging by intramolecular hydrogen. Using C5HF7, we have fabricated dual damascene structures in various low-k dielectrics ranging from k2.7 to 2.4. In addition, we have recently demonstrated low-k etch at 7nm node with superior profile control compared to C4F8-based etch. In this talk, we investigate the reasons behind the improved etch performance using C5HF7 compared to other passivation gases and potential future applications.

5:20pm **PS1-TuA10 First-Principles Theoretical Investigation on Mechanism of New Transition Metal Etching Process using Oxygen and argon Neutral Beams and Ethanol Gas**, ***Tomohiro Kubota**, Y. Kikuchi, S. Samukawa*, Tohoku University, Japan

Anisotropic and damage-free etching of transition metals (especially magnetic materials) is important for realization of MRAM. However, it is generally difficult to etch such materials with conventional plasma etching and Ar ion milling has been widely used which causes problems such as damage, re-deposition, and etc. Recently Gu et al. reported [1] that anisotropic and damage-free etching of transition metal (Ta, Ru, and Pt) is possible based on complex reaction of transition metal by introduction of ethanol gas and irradiation of argon/oxygen neutral beam [2]. It is expected the process proceeds as following: (1) metal surface is oxidized by bombardment of oxygen neutral beam, (2) ethanol molecules adsorb at the surface, and (3) metal complex like $Ta(OC_2H_5)_5$ is formed by argon neutral beam bombardment. However, detail of the mechanism (especially, why oxidation is needed) was not clear. To understand the etching mechanism, computational investigation was performed using first principle calculation.

Calculations based on density functional theory and cluster model were performed using a SGI UV1000/2000 system in Institute of Fluid Science, Tohoku University.

First, adsorption of ethanol on tantalum oxide and metallic tantalum was investigated. As a result, it was found that ethanol adsorbs spontaneously on both surfaces. It means that adsorption step is not a reason why oxidation is needed for the etching.

Then, we investigated possible reaction which may occur after the adsorption of ethanol. It was found that O–H bond in the adsorbed ethanol can be dissociated, the H can be moved, and a new O–H bond can be formed between an oxygen atom in the metal oxide and the dissociated hydrogen (hydrogen movement). This should cause dissociation of Ta-O bonds in the oxide to proceed etching. Note that this process should not occur at metallic tantalum surface because it does not have oxygen atom to accept the moving hydrogen, and this should be the reason why oxidation is needed for etching.

Furthermore, it was found that collision of argon caused the hydrogen movement reaction mentioned above. It means that the hydrogen movement reaction and possibly tantalum etching can occur in the experimental condition under argon neutral beam irradiation.

Acknowledgement: We thank Dr. Nozawa from Tokyo Electron Ltd. for valuable discussions.

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5:40pm **PS1-TuA11 Generalized Approach for Selecting Viable Plasma Chemistries in Patterning Magnetic Metals**, ***Jack Kun-Chieh Chen****, *T. Kim, N.D. Altieri, J.P. Chang*, University of California Los Angeles

As advanced memory devices begin to dictate the adoption of complex magnetic and multiferroic materials, overcoming the challenge of achieving high-fidelity patterning for these multifunctional films becomes imperative. Physics- and chemistry-based modeling affords tremendous understanding of elementary reaction mechanisms in plasma patterning; however, the parameters necessary for kinetic modeling are sometimes difficult to obtain experimentally for novel multifunctional compounds. Developing a comprehensive framework for selecting viable chemistries in plasma patterning of magnetic metals has the potential to reduce the time and cost associated with design of experiments.

In this work, a generalized methodology, combining thermodynamic assessment of various etching chemistries and kinetic verification of etching efficacy, is proposed. To screen various chemistries, reactions between the dominant vapor phase/condensed species at various partial pressures of reactants are first considered. The volatility of etch product is determined to aid the selection of viable etch chemistry. Magnetic tunnel junction (MTJ) based MRAM (Magnetic Random Access Memory) was used as a case study to address the challenge of patterning constituent materials of multilayers. Ar ion beam milling was a traditional method in patterning MRAM devices; however, sidewall re-deposition results in electrical shorts as the features become smaller with higher aspect ratios. Selected metals (Fe, Co, Pt) and their alloys within the MRAM were studied by the generalized approach. To validate the thermodynamic calculation, films were patterned using a modified reactive ion etch process of halogen discharge with subsequent H_2 plasma exposure. To further improve selectivity to mask materials, a separate novel method of surface modification using Ar ion beam assisted chemical etch (IBACE) was then investigated.

The etch rate of Fe, Co, and Pt were enhanced 40%, 25%, and 20% respectively with secondary H_2 chemistry. X-ray photoelectron spectroscopy (XPS) suggested chemical removal of non-volatile metal chlorides by H_2 plasma. Moreover, characterization through superconducting quantum interference device (SQUID) proved that coercive field strength of magnetic alloy after Cl_2 plasma can be recovered by additional H_2 plasma exposure from 63.6 to 20.9 Oe. Etching of metals and alloys was further examined in organic solution by mass spectroscopy to verify formation of organometallic complexes predicted by thermodynamics. IBACE, a vacuum-compatible process was developed and proven to be effective in patterning magnetic metal stacks.

6:00pm **PS1-TuA12 Short- and Damage-Free Process for Patterning Magnetic Tunnel Junctions for High-Density Application**, ***Dunja Radisic**, L. Souriau*, IMEC, Belgium, *V. Paraschiv,* SC Etch Technology Solutions, *D. Goossens,* IMEC, Belgium, *F. Yamashita, N. Koizumi, S. Tahara, E. Nishimura,* Tokyo Electron Miyagi Limited, Japan, *W. Kim, G. Donadio, D. Crotti, J. Swerts, S. Mertens, T. Lin, S. Couet, D. Piumi, GS. Kar, A. Furnemont*, IMEC, Belgium

The short- and damage-free patterning still remains the major challenge for the STT-MRAM high-volume commercialization. High-volume reactive ion etching (RIE) based short- and damage- free magnetic tunnel junction (MTJ) patterning was developed and electrically tested for isolated devices of sizes starting from 200nm down to 75nm and below. There was a tight TMR distribution measured after patterning (standard deviation of 7-14% was achieved) indicating that the process was short-free and it had no detrimental effect on the stack magnetic performance. In addition, measured TMR showed no significant size dependence, i.e., the TMR value was in the same, constricted range, for devices of different sizes. The process yield was 100%, meaning that all of the measured devices were functional and fitting the narrow TMR distribution.

The basic patterning sequence consisted of noble gas-based dry etch in RIE reactor followed by an in-situ SiN encapsulation in the RLSA reactor (both from Tokyo Electron Limited). MTJ stack was CoPt-based bottom pin with perpendicular anisotropy. Either TiN or Ta was used as a hard mask for etching. The stack was partially etched using medium bias process which resulted in some metallic re-deposition on the sidewalls. The remaining stack was etched and the sidewall residues efficiently removed using the high bias process step. For both steps, only noble gasses were used, so that the damage by reactive plasma species was prevented. The device performance dependency on the temperature in RIE reactor was studied by using either -20ºC or 60ºC ESC. The effect of the post-etch oxidation, aimed to convert possible metallic remains on the sidewalls into non-conductive metal oxides, was also tested. The in-situ SiN encapsulation was applied after etching to prevent possible stack properties modifications due to interaction with the atmosphere. The in-situ etch and deposition capability allowed for patterning sequences where multiple etching and deposition steps were combined. The approach with whole stack etch followed by encapsulation, as well as the approach with partial stack etch (down to MgO), followed by SiN spacer formation, remaining stack etch and final SiN encapsulation were used. In the second case, the SiN spacer formed after etching stopping in MgO was intended to act as a dielectric medium preventing the shorts caused by re-deposition.

The best device performance was achieved by using Ta HM, approach with partial etching stopping in MgO, spacer formation, followed by the remaining stack etching and final encapsulation. The oxidation steps were applied after etch stopping in MgO, and after etching of remaining MTJ stack.

*** Coburn & Winters Student Award Finalist**

Plasma Science and Technology
Room: 210B - Session PS2-TuA

Plasma Modeling
Moderator: Saravanapriyan Sriraman, Lam Research Corporation

2:20pm **PS2-TuA1 Realistic Plasma Etch Simulation for High Aspect Ratio Contact Hole using Graphics Processing Units**, ***Yeon Ho Im***, Chonbuk National University, Republic of Korea **INVITED**

With the continuous decrease in nanoscale design dimensions, semiconductor plasma processing is confronting the limits of physicochemical fabrication routes at the atomic scale. Especially, one of the emerging challenges is to achieve the ideal high-aspect ratio nanostructures without abnormal profiles, such as cylinder capacitors, shallow trench isolation, through-silicon vias. In spite of significant contributions of research frontiers, these processes are still unveiled due to their inherent complexity of physicochemical behaviors, and gaps in academic research prevent their predictable simulation. To overcome these issues, a Korean plasma consortium began in 2009 with the principal aim to develop a realistic and ultrafast 3D topography simulator of semiconductor plasma processing coupled with zero–D bulk plasma models. In this work, aspects of this computational tool are introduced. The simulator was composed of a multiple 3D level-set based moving algorithm, zero-D bulk plasma module including pulsed plasma processing, a 3D ballistic transport module, and a surface reaction module. The main rate coefficients in bulk and surface reaction models were extracted by molecular simulations or fitting experimental data from several diagnostic tools in an inductively coupled fluorocarbon plasma system. Furthermore, it is well known that realistic ballistic transport is a simulation bottleneck due to the brute-force computation required. In this work, effective parallel computing using graphics processing units was applied to improve the computational performance drastically. Finally, it is demonstrated that 3D feature profile simulations coupled with bulk plasma models can lead to better understanding of abnormal behaviors, such as necking, bowing, etch stops and twisting during high aspect ratio contact hole etch.

3:00pm **PS2-TuA3 Validation of Inductively Coupled Plasmas Sustained in Halogen Chemistries**, ***Ankur Agarwal***, Applied Materials Inc., *M. Foucher*, LPP-CNRS, Ecole Polytechnique, France, *S. Rauf*, Applied Materials Inc., *J.-P. Booth, P. Chabert*, LPP-CNRS, Ecole Polytechnique, France, *K.S. Collins*, Applied Materials Inc.

The growing complexity of industrial plasma processing systems and increasingly stringent technological requirements for plasma processes have necessitated the use of modeling and simulation for design of these systems in recent years. Impressive advances have been made in the development of computer models for plasma equipment design[1,2] and feature profile evolution.[3,4] Validation of these models with experimental data over a wide range of operating conditions is a critical step in making these models a mature development tool. While plasma equipment models have been benchmarked with ion/electron density measurements[5], RF and DC self-bias voltages[6], characterization of neutral species in industrially relevant chemistries is complicated and hence few benchmarking opportunities exist. Characterization of neutral species is critical as they serve as the precursors to any plasma etching (and deposition) process and are an important parameter for plasma equipment models to quantify for use in feature profile models.

In this work, we report on validation of Applied Materials' fluid plasma model, CRTRS, in an inductively coupled plasma (ICP) reactor sustained in halogen chemistries. Halogen-based ICPs are typically used to etch shallow trench isolation (STI) features and defining gate structures in both logic and memory devices. The density of Cl atoms in Cl_2 chemistries (or Br in HBr chemistries) is an important parameter to characterize the etching process. Recently, researchers have reported on electron and absolute Cl densities and gas temperature in a Cl_2 ICP reactor over a wide range of operating conditions.[7] The fluid plasma model was validated against these experiments for an ICP sustained in Cl_2 and Cl_2/O_2 mixtures over a pressure range of 10 mTorr to 90 mTorr and varying ICP power of 200 W to 500 W. We found gas temperature to be an important parameter to accurately predict the electron and atomic Cl densities as it governs the kinetics of gas phase chemistry and also affects diffusion coefficient.

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3:20pm **PS2-TuA4 Enhanced SiN Etching by Hydrogen Radicals during Fluorocarbon/Hydrogen Plasma Etching; Molecular Dynamics Simulation Analyses**, ***Yuichi Murakami***, *M. Isobe, K. Miyake,* Osaka University, Japan, *M. Fukasawa, K. Nagahata,* Sony Corporation, *T. Tatsumi,* Sony Corporation, Japan, *S. Hamaguchi*, Osaka University, Japan

Selective etching of silicon nitride (SiN) over silicon dioxide (SiO_2) or vice versa has been widely used in microelectronics fabrication processes. Plasmas derived from fluorocarbon (FC) gas with hydrogen (H_2) and/or hydrofluorocarbon (HFC) gas are typically used for etching processes of SiN. Our recent study using molecular dynamics (MD) simulations on surface reactions of SiN and SiO_2 with incident CHF_2^+ and CF_2^+ ions supplied by a HFC or FC/H_2 plasma has found that hydrogen supplied from incident ions inhibits the formation of FC polymer on the SiN surface during the process, which facilitates the formation of volatile SiF_x species on the SiN surface and therefore enhances its sputtering yield [1]. In the present study, we have also examined whether hydrogen reacts with a SiN or SiO_2 surface directly, by supplying more hydrogen to SiN and SiO_2 surfaces in MD simulations. An earlier experimental study [2] has showed that the SiN sputtering yield increases as the supply of hydrogen to the CF plasma increases. Following such an experiment, in this study, we have varied the amount of hydrogen radicals supplied to the SiN and SiO_2 surfaces and examined how their sputtering yields by CF_x^+ ions change, depending on the amount of hydrogen adsorbed on the surfaces. Detailed examinations of desorbed species and surface chemical compositions obtained from MD simulations of such processes have indicated that hydrogen in FC/H_2 plasmas react with nitrogen of the SiN surface to form volatile NH_x, most dominantly NH_3, to promote the surface etching whereas it hardly affects the sputtering yield of SiO_2 under the same conditions.

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4:20pm **PS2-TuA7 Plasma-induced Surface Roughening and Ripple Formation during Plasma Etching of Silicon**, ***Kouichi Ono***, Kyoto University, Japan **INVITED**

Atomic- or nanometer-scale surface roughness has become an important issue in the fabrication of nanoscale devices, because the roughness at feature sidewalls and bottom surfaces affects the variability in transistor performance. A better understanding of the mechanisms for the plasma-induced surface roughening is indispensable for suppressing the evolution of the roughness during plasma etching; moreover, the surface roughening through plasma exposure is positively employed in some cases, to obtain surface nanostructures such as nanopillars and nanocolumns. This paper presents a numerical and experimental study of surface roughening and ripple formation during Si etching in Cl-based plasmas, with emphasis on modeling, analysis, and control of the plasma-surface interactions concerned. A three-dimensional atomic-scale cellular model (ASCeM-3D) based on the Monte Carlo algorithm, which was developed to simulate plasma-surface interactions and the feature profile evolution during plasma etching, exhibited the nanoscale surface roughening and rippling in response to ion incidence angle onto substrate surfaces [1]: randomly roughened surfaces at normal incidence, and ripple structures or slit-like grooves perpendicular and parallel to the direction of ion incidence at oblique and grazing incidences, respectively. Such roughening and rippling of etched surfaces were found to be crucially affected by the ion scattering or reflection on microscopically roughened feature surfaces. Experiments of the surface roughening during Si etching in inductively coupled Cl_2 plasmas showed roughening and smoothing (or non-roughening) modes which occur depending on ion incident energy [2]. The analysis with the help of plasma diagnostics and the ASCeM-3D and classical molecular dynamics (MD) simulations [3] indicated that these two different modes of surface roughening correlate essentially to changes in the predominant ion flux from ions with high reflection probabilities to those with lower ones on surfaces on incidence at increased ion energy. The experiments further demonstrated that the pulse-biasing is effective for reducing the surface roughness during plasma etching, and the surface rippling with oblique and grazing ion incidences onto substrate surfaces was demonstrated using a sheath-control plate placed thereon.

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5:00pm **PS2-TuA9 Feature Scale Modeling of Semiconductor Processes**, ***Phillip Stout***, Applied Materials **INVITED**

An overview of monte carlo feature scale modeling work will be presented. The two major areas of discussion will be etching and metallization processes.

In high aspect ratio (HAR) oxide etch processes the mask gates the amount of etchants and passivants entering the feature and has a large influence on the resulting etched profile. Mask sidewall slopes alter the path of ions entering the feature thereby modifying the ion strike map inside the feature. Mask geometry also influences polymer deposition within mask and bow formation in oxide. Mechanisms for off-axis profiles and profile distortion include: off-axis ion incidence to wafer, non-uniform polymer deposition at opening, re-deposition of etch byproducts, feature geometry (mask), mask reflow, charging in feature, and off-angle yield curve peaks. Two cases illustrate the interplay of these profile distortion mechanisms: pattern distortion dependence on etch stop layer charging properties, and the influence of a tilted hard mask on HAR trench oxide etch profile. Feature scale models can be used to study integration issues in multi-step processes. A thirteen step spacer double patterning integration has been studied showing the importance of the spacer etch step. An STT-MRAM (Spin Transfer Torque - Magnetoresistive Random Access Memory) etch process will be discussed. Removal of metal sidewall deposits resulting from re-deposition of sputtered MTJ metal layers is a major issue. The study looks at ion beam etching.

The metallization topics reviewed will inlcude copper physical vapor deposition (PVD) in dual-damascene (DD) features, predicting across wafer coverage in feature, and copper reflow studies. In DD features a sloped inner via sidewall can have faster yields than the trench bottom. With reactor models supplying across wafer flux and aedfs it is possible to predict feature coverage properties as a function of wafer position. With smaller feature sizes copper reflow is being explored as a means to fill via and trench structures for back end of line interconnects. Using a simple hopping surface diffusion model, reflow behavior is shown. The model predicts the initial reflow causes rounding of the Cu surfaces and a shrinking of the opening as the surfaces round to a more minimal surface configuration.

5:40pm **PS2-TuA11 Pattern Loading in Etch through Profile Simulation**, ***Yiting Zhang***, *S. Sriraman*, *J. Belen*, *A. Paterson,* Lam Research Corporation, *M.J. Kushner*, University of Michigan, Ann Arbor

Pattern transfer in microelectronics fabrication extensively uses plasma-assisted etching processes. Optimization of etch processes for 3D structures, such as FinFETs and Tri-Gate transistors, utilized in current technology nodes is considerably more difficult. For example, etching of 3D structures and mask layouts typically require longer over-etch process time to clear material, especially in corners, introducing additional selectivity challenges to maintain feature scale critical dimensions (CDs). In addition, feature open area, feature orientation, and proximity to other nearby structures can influence process etch outcomes. While for past technology nodes, 2D etch profile models were sufficient to optimize features and connect reactor scale properties to feature evolution, 3D structures are not well represented by 2D profile simulations.

In this paper, we report on the recent development and progress of a 3D profile simulator: the Monte Carlo Feature Profile Model (MCFPM-3D). The modeling platform in MCFPM-3D includes many advanced features such as charging, mixing, implantation, and photon-stimulated processes. The model addresses reaction mechanisms resulting in etching, sputtering, mixing, and deposition on the surface to predict profile evolution based on fluxes of radicals, ions, and photons provided by an equipment scale simulator. In these studies, energy and angularly resolved fluxes are provided by the Hybrid Plasma Equipment Model (HPEM). Results from profile simulations of feature pattern loading in etching of 2D and 3D structures will be presented. Phenomena such as reactive ion etch lag and aspect ratio dependent etching will be discussed.

6:00pm **PS2-TuA12 Plasma Modeling of a Magnetized Inductively-Coupled Plasma Reactor**, ***Jason Kenney***, *S. Rauf*, *K.S. Collins*, Applied Materials, Inc.

Modification of plasma properties with applied magnetic fields is fundamental to the study of plasma physics. In plasma reactor design, magnetic fields are regularly employed to modify plasma density profiles, e.g. as a tuning knob for plasma processing applications or as a means to prevent wall losses through confinement. Recently [1,2], their impact on electron energy distributions has also been measured and modeled in inductively-coupled plasma (ICP) systems.

In this work, we consider the application of static magnetic fields in an ICP reactor using a 2D fluid plasma model [3]. The model has been updated to include solution of the 3D inductively-coupled electric field components in the presence of a static 2D magnetic field [4] and has appropriate modification of electron mobility and diffusion coefficients to their tensor forms. We investigate the impact of magnetic field structure and strength on plasma density profile, electron temperature, ion energy distribution, and plasma chemistry for a variety of processing conditions (pressures, powers, feedstock gases), focusing on both the region near the ICP source and in close proximity to the processing stage. We also consider the form and intensity of electric field components and impact on power deposition region when a magnetic field is applied and discuss model validation with peer-reviewed experimental data.

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Advanced Surface Engineering
Room: 212A - Session SE+PS-TuA

Pulsed Plasmas in Surface Engineering
Moderator: Jolanta Klemberg-Sapieha, Ecole Polytechnique de Montreal, Canada, Michael Stueber, Karlsruhe Institute of Technology

2:20pm **SE+PS-TuA1 Strategy for Tuning the Average Charge State of Metal Ions Incident at the Growing Film during HIPIMS Deposition**, ***Grzegorz Greczynski***, Linköping University, Sweden, *I. Petrov,* University of Illinois at Urbana Champaign, *J.E. Greene,* University of Illinois at Urbana-Champaign, *L. Hultman*, Linköping University, Sweden

Energy- and time-dependent mass spectroscopy is used to determine the relative number density of singly- and multiply-charged metal ions incident at the substrate during high-power pulsed magnetron sputtering (HIPIMS) as a function of the average noble-gas ionization potential. We selected Ti as the sputtering target since the microstructure, phase composition, properties, and stress-state of Ti-based ceramic thin films grown by HIPIMS are known to be strongly dependent on the charge state of Ti^{n+} (n = 1, 2, …) ions incident at the film growth surface. [1,2] Mass spectroscopy results show that the flux of Ti_{n+} with $n > 2$ is insignificant; thus, the $\mathrm{Ti}_{2+}/\mathrm{Ti}_{+}$ integrated flux ratio $J_{Ti}{}^{2+}/J_{Ti}{}^{+}$ is measured at the substrate position as a function of the choice of noble gas -- Ne, Ar, Kr, Xe, as well as Ne/Ar, Kr/Ar, and Xe/Ar mixtures -- supporting the plasma. We demonstrate that by changing noble-gas mixtures, J_{Ti2+} varies by more than two orders of magnitude with only a small change in J_{Ti+}. This allows the ratio $J_{Ti}{}^{2+}/J_{Ti}{}^{+}$ to be continuously tuned from less than 0.01 with Xe, which has a low first-ionization potential IP^1, to 0.62 with Ne which has a high IP^1. The value for Xe, $IP^1{}_{Xe}$ = 12.16 Ev, is larger than the first ionization potential of Ti, $IP^1{}_{Ti}$ = 6.85 Ev, but less than the second Ti ionization potential, $IP^2{}_{Ti}$ = 13.62 Ev. For Ne, however, $IP^1{}_{Ne}$ = 21.63 Ev is greater than *both* $IP^1{}_{Ti}$ and $IP^2{}_{Ti}$. Therefore, the high-energy tail of the plasma-electron energy distribution can be systematically adjusted, allowing $J_{Ti}{}^{2+}/J_{Ti}{}^{+}$ to be controllably varied over a very wide range, from 0.01 with Xe to 0.62 with Ne. [3]

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2:40pm **SE+PS-TuA2 Study of High Power Pulsed Magnetron Sputtering Under Differing Magnetic Field Configurations**, ***Priya Raman***, *I.A. Shchelkanov*, *J.T. McLain,* University of Illinois at Urbana Champaign, *S. Armstrong,* Kurt J. Lesker Company, *D.N. Ruzic*, University of Illinois at Urbana Champaign

There is an increasing demand for high quality, wear-resistant, low-friction and corrosion resistant coatings in the microelectronics, automotive, tooling and other industries. High power magnetron sputtering is a type of magnetron sputtering technique where short high power pulses are applied to the magnetron target at very low duty cycles leading to higher degree of ionization of the target material. These ionized sputtered material assist in film growth leading to more adhesive, dense, and smoother films compared to conventional DC Magnetron Sputtering (dcMS) techniques. Unfortunately HPPMS suffers from lower deposition rates due to “return effect” of the ionized sputter materials [1]. Further reach of the HPPMS technology largely depends on whether it can produce deposition rates comparable or higher than dcMS. Recent studies of HPPMS discharges have shown that the magnetic field in the region above the sputter target defines the plasma properties and potential distribution in that region. The "ε" magnet pack [2] had already demonstrated increased deposition rates by carefully changing the magnetic field pattern above the target surface. Cylindrically symmetric "TriPIMS" magnet was developed based on magnetic field design solutions from "ε" magnet pack to keep the high deposition rates but improve deposition uniformity. In order to fully understand the behaviour of high current pulsed discharge in this new magnetic field configuration, TriPIMS magnet pack, was tested with Huettinger HiPIMS, Z-pulser MPP, Starfire Impulse and DC power supplies. Plasma parameters (ne, Te, ionization fraction), deposition rate, deposited film density, uniformity, and stress were measured. Reason for higher deposition rate is discussed.

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3:00pm **SE+PS-TuA3 Reactive High-power Impulse Magnetron Sputtering and Pulsed Magnetron Co-sputtering of Multifunctional Films**, ***Jaroslav Vlcek***, *J.R. Rezek, P.M. Mares*, University of West Bohemia, Czech Republic **INVITED**

In the presentation, we report on discharge and deposition characteristics (including the ion flux characteristics at the substrate), and on film structure and properties for two different pulsed reactive magnetron sputtering techniques.

High-power impulse magnetron sputtering (HiPIMS) with a pulsed reactive gas flow control was used for high-rate reactive depositions of densified, highly optically transparent, stoichiometric ZrO_2 and HfO_2 films, and of Ta-O-N films with tunable composition and properties. The depositions were performed using a strongly unbalanced magnetron with a planar directly water-cooled Zr, Hf or Ta target in $Ar-O_2$ or $Ar-O_2-N_2$ gas mixtures at an average target power density of up to 2.4 $kWcm^{-2}$ in a pulse. The repetition frequency of pulses was 500 Hz at 50 – 200 μs voltage pulse lengths and the total pressure close to 2 Pa. An effective reactive gas flow control made it possible to produce high-quality ZrO_2, HfO_2 and Ta-O-N films with high deposition rates (up to 120 nm/min, 345 nm/min and 190 nm/min, respectively, for the target-to-substrate distance of 100 mm) and to adjust the composition of the Ta-O-N films from Ta_2O_5 to a mixture of Ta_3N_5 and TaN. We prepared almost stoichiometric TaON films possessing appropriate band-edge levels for water splitting and a narrow optical band gap of 2.5 eV that permits a visible light absorption up to 500 nm. Selected results obtained using a parametric model for the controlled reactive HiPIMS of the ZrO_2 films are presented.

Pulsed dc magnetron co-sputtering of a single segmented target (B_4C-M, where M = Ti, Zr and Hf, or B_4C-Hf-Si) in Ar gas or $Ar-N_2$ gas mixtures was used for deposition of different multifunctional films. The repetition frequency of pulses was 10 kHz at a fixed 85 μs voltage pulse length and the total pressure of 0.5 – 1.7 Pa. Energy-resolved mass spectroscopy was used to correlate the energy of Ar^+ ions bombarding the growing films with high positive voltage overshoots after the negative voltage pulses and with the energy of Ar atoms backscattered from the sputtered targets. We present the results obtained for nanocolumnar ZrB_2-type Zr-B-C films and nanocomposite Zr-B-C-N films exhibiting a high hardness (37 GPa) and high electrical conductivity, and for nanostructured HfB_2-type Hf-B-Si-C films with a high hardness (34 – 37 GPa), high electrical conductivity and significantly improved oxidation resistance in air up to 800 °C.

4:20pm **SE+PS-TuA7 Target Poisoning in Mixed Ar, N_2 and CH_4 Atmosphere, in Processes Using Different Target Materials for HIPIMS/DC and DC Cathode Modes.**, ***Anna Oniszczuk***, *A.P. Ehiasarian*, Sheffield Hallam University, United Kingdom of Great Britain and Northern Ireland, *C.F. Carlström, M. Ahlgren*, Sandvik Coromant, Sweden

Reactive sputtering in mixed $Ar+N_2+CH_4$ atmosphere is a widely used industrial process however the poisoning of different target materials under different sputtering discharges in this complex environment is insufficiently described.

In mixed $Ar+CH_4+N_2$ atmosphere, at low flow processes were influenced by methane whereas at high flow they were dominated by nitrogen indicating the formation of carbide and then carbonitride compounds. This was observed for both TiAl and V targets in DC as well as in HIPIMS mode.

Vanadium targets operating in DC mode were poisoned at 55% of reactive gas flow. Poisoning resulted in a 2-fold increase in total pressure, a 50 % increase in discharge voltage/current ratio, a 5 fold drop in V(I) optical emission intensity and a 10 fold drop in V^+ and Ar^+ fluxes obtained from energy-resolved mass spectroscopy.

TiAl targets in DC mode poisoned at lower reactive gas flows and exhibited narrower hysteresis than V due to the higher reactivity of the target material. The voltage/current ratio of TiAl targets went through a minimum with a flow, while for V target it increased with flow.

For HIPIMS both targets poisoned earlier and the hysteresis was narrower than in DC mode. As confirmed by trends in the partial pressure, the voltage/current ratio and ion fluxes of metals and reactive gasses. These effects are due to higher reactivity of the plasma as evidanced by higher fluxes of N^+ and N_2^+ and radicals containing H, C and N. The voltage/current ratio reduced by 50% as the target is poisoned in contrast to operation in DC mode where it increased. This could be attribiuted to efficient ionization and drop in plasma impedance.

Pathways for poisoning and resulting ion fluxes are discussed.

4:40pm **SE+PS-TuA8 Structure and Properties of Cr_2O_3 Coatings Deposited using DCMS, PDCMS, and DOMS**, ***Jianliang Lin***, Southwest Research Institute, *W.D. Sproul*, Reactive Sputtering, Inc.

The properties of oxide coatings are strongly tied to the crystallinity of oxide phases. In general, a well-crystallized oxide phase is desired because it is usually related to improved mechanical and chemical properties. This paper presents a comparative study of the chromium oxide (Cr_2O_3) coatings deposited by deep oscillation magnetron sputtering (DOMS), mid-frequency pulsed dc magnetron sputtering (PDCMS) and continuous dc magnetron sputtering (DCMS). Without applying external substrate heating, the processing techniques strongly affected the crystallinity of the Cr_2O_3 coatings. The DCMS-Cr_2O_3 coating exhibited an amorphous like structure. The coating deposited by PDCMS contained a mixture of amorphous and crystalline phases. In contrast, the DOMS-Cr_2O_3 coating showed a strong crystallinity with a (110) preferential orientation. The improved crystallinity of the DOMS-Cr_2O_3 coating is due to the higher ion bombardment and higher substrate saturation temperature, which is related to the high energy electron bombardment associated with deep oscillation pulses. Improved mechanical properties and wear resistance were achieved in the DOMS-Cr_2O_3 coatings as compared to the coatings deposited using DCMS and PDCMS. This study also showed that the bias voltage strongly affected the structure of the DOMS-Cr_2O_3 coatings by changing the substrate current characteristics.

5:00pm **SE+PS-TuA9 Strategy to Tailor the Composition of Silicon Oxynitride Thin Films Deposited by Reactive High Power Impulse Magnetron Sputtering using Nitrous Oxide as a Single-source Precursor**, ***Tuomas Hänninen***, *S. Schmidt, J. Jensen, L. Hultman, H. Högberg*, Linköping University, Sweden

Silicon oxynitride (SiON) is a material with tunable optical and electrical properties. It is used as thin films in antireflection coatings, surface passivation layers, and optical waveguides. Commonly two reactive gases, O_2 and N_2, have been employed for the reactive magnetron sputter deposition of SiON. The two-gas approach is, however, limited by the non-linear target effects as a function of reactive gas flow rates, which makes an accurate control of the deposition process challenging.

In this study we present SiON thin films deposited by reactive high power impulse magnetron sputtering from a pure Si target in Ar/N_2O plasmas. The influence of the average target power while maintaining a fixed pulse frequency (1000–4000 W at 1000 Hz and 1200–3000 W at 600 Hz) and the frequency at a fixed energy per pulse (300–1000 Hz at 4 J) on the resulting film properties were investigated.

The ~ 300 nm thick films show a dense and featureless morphology when viewed in cross-sectional scanning electron microscopy. X-ray diffraction reveals that the films are X-ray amorphous and exhibit compressive residual stresses in the range of 500–1500 Mpa. The chemical bonding structure and the elemental composition of the films were studied with X-ray photoelectron spectroscopy. The spectra acquired from the as-deposited samples show mixed Si—O, Si—N, and Si—Si bonding. The ratio between these type of bonds correlates with the atomic concentrations of Si, O, and N in the films. A decreased average power at a fixed pulse frequency induces an increase in O content (from 13 at.% to 51 at.% at 1000 Hz and from 17 at.% to 43 at.% at 600 Hz) while the N concentration remains virtually unaffected. An exception are films with the highest O content, showing a decrease in N content from ~ 26 at.% to 9 at.% at 1000 Hz and to 16 at.% at 600 Hz. A similar behavior is observed when the pulse frequency is lowered at a constant pulse energy, the film O content increases from 13 at.% to 43 at.%, followed by a decrease in N concentration from ~ 26 at.% to 17 at.%. Film densities as measured by X-ray reflectivity are found to range between 2.6–2.9 g/cm^3. The refractive indices and extinction coefficients at 633 nm, measured by variable-angle spectroscopic ellipsometry, show that the films with highest total O plus N content have the lowest refractive index (1.6–1.8) and extinction coefficient (~ 0) values. The refractive index values are comparable to those of SiO_2 (~ 1.45) and

Si_3N_4 (~ 2.0), confirming that the optical properties of the studied films can be tailored to range between SiO_2 and Si_3N_4.

5:20pm **SE+PS-TuA10 Phase Changes Observed on AlCr Composite Cathodes due to the Exposure to Cathodic Arc Plasmas in N_2 and O_2 Atmospheres**, ***Robert Franz***, *F. Mendez Martin, G. Hawranek*, Montanuniversität Leoben, Austria, *P. Polcik*, PLANSEE Composite Materials GmbH, Germany

Hard and wear-resistant coatings based on the system aluminium and chromium represent the state of the art in the protection of tools used in metal cutting operations. Using cathodic arc deposition techniques in nitrogen and/or oxygen atmospheres, nitrides, oxides or oxynitrides can be synthesised. The growth conditions encountered in processes employing cathodic arc plasmas are typically characterised by a high degree of ionisation and high deposition rates. For the supply of the non-gaseous elements during the deposition, it is common to use multi-element cathodes containing the desired Al/Cr ratio. These cathodes are usually composite cathodes and are widely used in industrial-scale deposition systems since they facilitate an easier process control and reproducibility. However, the plasma conditions in the cathodic arc plasma using such multi-element cathodes and their erosion behaviour in reactive atmospheres are only scarcely studied.

In the present investigation, AlCr composite cathodes with compositions of 75/25, 50/50 and 25/75 at.-% were exposed to cathodic arc plasmas in N_2 and O_2 atmospheres. Due to periodic melting and solidification of the cathodes' near-surface region in the cathode spots, an intermixing of the elements Al and Cr and the formation of intermetallic phases occurred which was analysed by recording elemental distribution maps in the cross-sections using scanning electron microscopy. By comparing regions of strong erosion with areas less affected by the cathodic arc plasma, poisoning effects due to reactions of the metals in the cathodes and the background gas could be identified and were analysed in detail. The conductivity of the formed nitrides and oxides on the surface of the AlCr composite cathodes was decisive for the characteristics of the cathodes' erosion behaviour. All results regarding the cathode erosion and the phase changes are compared to similar studies on TiAl [1] and $Al_{0.7}Cr_{0.3}$ [2, 3] cathodes and are put in context with recently reported arc plasma properties obtained with the same AlCr cathodes and gas atmospheres [4, 5].

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[4] R. Franz, P. Polcik, A. Anders; *IEEE Trans. Plasma Sci.* 41 (2013) 1929–1937

[5] R. Franz, P. Polcik, A. Anders; *Surf. Coat. Technol.* 272 (2015) 309–321

5:40pm **SE+PS-TuA11 Optimization of Linear Scanning Magnetron Array Performance**, ***Vladimir Kudriavtsev***, *A. Riposan, D.W. Brown, C. Smith, T. Bluck*, Intevac, Inc.

In this presentation we discuss Linear Scanning Magnetic Array (LSMA) technology for magnetron sputtering in conjunction with in-line substrate processing. In this approach, the magnet array (pole) scans over planar target spreading the erosion pattern in a controlled fashion. Thus, high quality, dense films with good uniformity can be produced at significant advantages over static magnetrons, such as significantly higher target utilization, longer uptime, and prevention/removal of target defects related to re-deposition.

We review the influence of magnet motion acceleration/deceleration, the influence of endpoint motion offset (stagger), and the influence of magnet - to - substrate velocity ratio, on target utilization and lead-to-trail edge film uniformity. Trade-offs between uniformity and target utilization were established and characterized.

The optimization method we use employs a combination of theoretical simulations and experimental measurements. Theoretical analysis utilizes ANSYS static magnetic field simulations, erosion profile calculations including motion integration effects, and ray tracing method for sputtering film thickness calculations (MATLAB). The structure and uniformity of LSMA-deposited thin films was characterized experimentally by XRF and SEM, and the target erosion measured by weight and erosion profiles of spent targets.

We have demonstrated that, with a judicious design approach, an optimal range of operating parameters can be defined and target utilizations above 70%can be reached, while maintaining deposition uniformity below 2% with excellent film properties. This makes the LSMA plasma source (using planar targets) more economically competitive than static and rotatable magnetrons.

6:00pm **SE+PS-TuA12 Correlation of Microstructure of Deposited Thin Films with Discharge Characteristics by Modulated Pulsed Power Magnetron Sputtering (MPPMS)**, ***M.K. Lei***, Dalian University of Technology, China

Pure Cu thin films and TiAlSiN nanocomposite thin films are deposited in a closed field unbalanced magnetron sputtering system using the modulated pulsed power magnetron sputtering (MPPMS), in order to understand the correlation of the microstructure and texture of deposited thin films with the discharge characteristics by MPPMS. The discharge processes at different pressures on the metallic targets are numerically modeled with considering the loss of electrons by cross-B diffusion. With increasing the pressure from 0.1 to 0.7 Pa, both the ion bombardment energy and substrate temperature which are estimated by the modeled plasma parameters decrease, corresponding to the observed transition of the deposited Cu thin films from a void free structure with a wide distribution of grain size into an underdense structure with a fine fiber texture in the extended structure zone diagram. The TiAlSiN thin films are deposited at the ratio of the nitrogen flow rate to the total gas flow rate (f_{N2}) ranging from 0 to 40%. An optimized nanocomposite structure of *nc*-TiAlN/*a*-Si_3N_4 is formed with the 5–10 nm TiAlN nanocrystallites embedded in the 2–3 nm amorphous Si_3N_4 matrix. Further increasing f_{N2}up to 40%, the grain size of nanocrystallites increase to 10–20 nm with the gradually precipitation of AlN phase, albeit the composition keeps constant. With increasing the partial pressure, the increased ion bombardment energy and substrate temperature are believed to be responsible for the complete phase separation of the *nc*-TiAlN/*a*-Si_3N_4 nanocomposite thin films.

Surface Science
Room: 113 - Session SS+AS+EN-TuA

Mechanistic Insight of Surface Reactions: Catalysis, ALD, etc. - II

Moderator: Bruce D. Kay, Pacific Northwest National Laboratory

2:20pm **SS+AS+EN-TuA1 How does Absorbed Hydrogen Drive Olefin Hydrogenation on Pd?**, ***Satoshi Ohno***, *M. Wilde, K. Fukutani*, The University of Tokyo, Japan

Pd-dissolved hydrogen is an essential ingredient in the highly selective hydrogenation of olefinic C=C double bonds catalyzed by Pd, yet the particular role played by H below the surface has long been debated controversially. Some proposed that absorbed H atoms become directly involved in hydrogenation reactions after they emerge from the metal interior onto the catalyst surface in an energetic state. Others considered that sizeable populations of subsurface sites by absorbed hydrogen indirectly activate surface-adsorbed hydrogen by altering the electronic structure of the catalyst.

To resolve this dispute we have studied the hydrogenation reaction of cis-2-butene to butane on a Pd(110) model catalyst surface with temperature-programmed desorption (TPD) and $^{1}H(^{15}N, \alpha\gamma)^{12}C$ nuclear reaction analysis (NRA) that reveals the hydrogen distribution on and beneath the surface. TPD demonstrates that the catalytic hydrogenation reaction proceeds efficiently between 160 and 250 K. NRA under the hydrogenation reaction condition, on the other hand, shows that the H concentration in the Pd subsurface region is as small as 0.5 at. %. Thus, the scenario of indirect surface-hydrogen activation through large quantities of H in the subsurface sites appears rather unrealistic for our experimental conditions. We furthermore elucidate that the butane reaction yield scales linearly with the number of Pd-dissolved H atoms that reach the surface after diffusion from the Pd bulk. This observation clarifies that the Pd-catalyzed olefin hydrogenation is triggered by the emergence of bulk-dissolved hydrogen onto the Pd surface. Our NRA H profiles also demonstrate that the catalytic reaction proceeds on the Pd surface fully saturated with chemisorbed hydrogen. This surface hydrogen is considered important, as it possibly prevents deactivation of reactive surface hydrogen species in vacant chemisorption sites.

Finally, the TPD spectrum of butene shows four peaks at 140, 165, 190, and 225 K, suggesting multiple butene-adsorption modes onto Pd(110) surfaces. Reactive TPD experiments in presence of absorbed hydrogen exhibit a significant decrease in the 165 K peak, identifying this feature as the reactive butene species in the catalytic hydrogenation reaction.

2:40pm **SS+AS+EN-TuA2 CO Oxidation over Pd Catalysts Supported on Different Low-Index Surfaces of CeO_2: A Combined Experimental and Computational Study**, ***Xiao Liu**, Y.W. Wen, Z.Z. Chen, B. Shan, R. Chen*, Huazhong University of Science and Technology, China

Pd/CeO_2 has attracted much attention on the low temperature CO oxidation due to the strong metal-support interactions. In this study, we have systematically investigated the interface properties and CO oxidation activities of Pd catalysts supported on different low-index surfaces of CeO_2. The Pd/CeO_2 nanorods have been prepared by incipient wetness impregnation method and the exposed surfaces of CeO_2 nanorods have been controlled by changing the calcination temperature after their successful synthesis by hydrothermal method. Their catalytic activities in CO oxidation have been tested and the results show that Pd catalysts supported on CeO_2 nanorods exposed by (100) and (110) (calcined at 500 ºC) are more activated than that exposed by (111) (calcined at 700 ºC), which is related to the surface oxygen vacancies concentration and the strength of interface interaction. By performing density functional calculations, the surface oxygen activities and the binding strength of Pd clusters on these low-index surfaces of CeO_2 have been investigated. The results show that the oxygen vacancy formation energies of (100) and (110) are smaller than that of (111). The binding strength of Pd clusters on these surfaces follows the sequence: (100) > (110) > (111). Furthermore, CO oxidation routes on these surfaces proceeding through the LH, ER and MvK mechanism have been studied. Our studies not only reveal that the catalytic performance of Pd/CeO_2 can be tuned by controlling the exposed surface of oxide but also shed light on the interface structures and CO oxidation mechanism of Pd/CeO_2 system.

3:00pm **SS+AS+EN-TuA3 *In Situ* Adsorption and Decomposition Studies of Dimethyl Methyl Phosphonate on Molybdenum Oxide Surfaces and Nanoparticles**, ***Ashley Head**, L. Trotochaud, Y. Yu*, Lawrence Berkeley National Laboratory (LBNL), *Z. Hicks, X. Tang, K. Bowen,* Johns Hopkins University, *B. Eichhorn,* University of Maryland, College Park, *H. Bluhm*, LBNL

There is great interest in understanding the interaction between the nerve agent simulant dimethyl methyl phosphonate (DMMP) and metal oxide surfaces to further nerve agent filtration technology and decomposition methods. To this end, we have studied the room temperature adsorption of DMMP on MoO_2 and MoO_3 surfaces up to 30 mTorr using ambient pressure x-ray photoelectron spectroscopy (APXPS). On both surfaces, the majority of DMMP adsorbs intact, but differences in the behavior of DMMP on the two substrates are found upon heating. Two phosphorus species are seen on the MoO_2 surface and three are seen on the MoO_3; these species remain on both surfaces up to 450 ºC Additionally, carbon remains on the MoO_2 at high temperatures but is removed from MoO_3 by 420 ºC. The APXPS data were correlated with TPD measurements of DMMP adsorbed on MoO_3 clusters on HOPG, a model system closer to real filtration materials. Methanol was found as the major decomposition product in addition to trace amounts of dimethyl ether. The easily reducible MoO_3 is likely responsible for an oxidative cleavage of the P-CH_3 bond on both the surface and nanoparticles. These studies highlight how APXPS coupled with TPD yields chemical information relevant to real-world applications.

3:20pm **SS+AS+EN-TuA4 Adsorption of Sterically Hindered Sulfur Containing Molecules on a Heterogeneous Model Catalyst**, ***Signe Sørensen**, J.V. Lauritsen*, Aarhus University, Denmark

Cobalt promoted MoS2 nanoclusters (CoMoS) are the active phase of the hydrodesulfurization catalyst which enables sulfur removal from crude oil. New legislations on sulfur impurity levels in diesel in EU and US demands still lower sulfur content which increases the requirements for even more effective catalysts.

Previously catalysts were improved by costly trial-and-error experiments. To target the improvements attempts, understanding of the catalytic mechanism is crucial. In the hydrodesulfurization catalysis the main source to residual sulfur content is the sterically hindered sulfur containing molecules, as the reactivity towards these is very low. To targeted enhance the catalytic activity, atomic scale understanding of this catalytic mechanism is essential.

Scanning tunneling microscopy (STM) is an outstanding tool for real space, atomic-scale imaging of supported nano-scale systems. This makes it the optimal tool for investigating the interaction between the sulfur containing molecules and metal-supported CoMoS, as it offers the unique and powerful ability to directly observe the catalytic active site by imaging single molecules adsorbing on the nanoparticles.

In this study STM is used on a model system of Co-promoted MoS2 on a gold substrate under ultrahigh vacuum conditions. To study the adsorption of the strongly steric hindered sulfur containing molecule 4,6-dimethyl-dibenzothiophene the molecule is dosed directly onto the nanoparticles which means that their location, orientation and the dynamics of single molecules can successfully be revealed through atom-resolved STM images and films. All observed adsorption modes are either associated with a sulfur vacancy on the corner site of the nanoclusters or with the one-dimensional metallic edge state associate with the edge of the Co-promoted MoS2 nanoclusters. These observations strongly indicate that these sites are important active sites of the catalyst and enable targeting the attempts for enhanced activity to optimization of the number of these apparent active sites in the industrial catalyst.

4:20pm **SS+AS+EN-TuA7 Metal Nanoparticles on Thin Film Oxide Supports: Interaction and Reaction of Metals with Hydroxyls**, ***Martin Sterrer***, University of Graz, Austria **INVITED**

Water-oxide interaction is of great importance in a number of technologically relevant fields, among them heterogeneous catalysis. Several studies report on the promoting effect of water in catalytic reactions, the participation of surface hydroxyls in catalytic reactions, and the influence of hydroxylation on the binding of metals to oxide surfaces. Achieving a fundamental atomic scale understanding of water-oxide interaction at environmentally and catalytically relevant conditions (e.g. ambient pressure) represents, therefore, a challenge for surface science studies related to heterogeneous catalysis. In this contribution, I will present results of our recent studies related to the interaction of water with thin, single crystalline oxide films (Fe-oxides, alkaline earth oxides) carried out in a wide range of water chemical potential (from UHV to mbar water pressures). Topics that will be discussed are the characterization of ordered water monolayers, the dewetting of ice on oxide surfaces, hydroxylation of oxide surfaces at elevated pressure, the influence of hydroxyls on metal nucleation and sintering, and metal deposition onto oxide surfaces from aqueous solutions.

5:00pm **SS+AS+EN-TuA9 Dynamics of Isolated Surface Complexes Formed Between a Chemisorbed Chiral Molecule and a Prochiral Reactant**, ***Jean-Christian Lemay**, Y. Dong, P.H. McBreen*, Laval University, Canada

Adsorbed chiral molecules (chiral modifiers) can interact stereoselectively with prochiral co-adsorbates on reactive metal surfaces (1). This is used in one of the most common methods to perform asymmetric heterogeneous catalysis. The chiral modifier provides stereoselection through non-covalent assembly with a substrate, forming isolated complexes with well-defined geometries. We will present a variable temperature STM study of individual bimolecular complexes formed by enantiopure 1-(1-naphthyl)ethylamine and three representative prochiral substrates on Pt(111). The results reveal sub-molecularly resolved and time-resolved stereospecific data for competing complexation geometries. Time-lapsed STM measurements of individual substrate molecules sampling a set of interaction geometries provide new insight on the dynamics of stereocontrol. The results reveal that a single prochiral substrate can probe various sites on the surface due to diffusion and prochiral switching. This shows the importance of considering interconversion between complexation geometries to fully understand the stereocontrol operated by the chiral modifier. The results will be discussed in the context of proposed mechanisms for enantioselective hydrogenation.

5:20pm **SS+AS+EN-TuA10 Density Functional Theory Study of CO Assisted Water Dissociation**, ***Liney Arnadottir**, L. Halberstadt*, Oregon State University

Previous computational studies of methanol oxidation reaction intermediates (H-C=O and C-OH) have shown significant effects of water on both adsorbate adsorption energy as well as activation energies of interconversion between the two. On a clean Pt(111) surface the interconversion between the two forms goes through a very stable COads and Hads intermediates and the activation barriers of CO + H to from HCO or COH are high or 1.3 and 1.8 eV respectively. In the presence of a single coadsorbed water molecule the activation barrier for this interconversion from HCO to COH was found to be much lower or 0.62 eV. These studies were motivated by experimental studies of methanol oxidation on Pt which found CO_2 formation at potentials lower then typically required for CO oxidation. Here we investigate Pt-water interactions and the effects of co-adsorbate CO on water dissociation as a possible CO assisted water dissection as an alternative reaction pathway on Pt surfaces.

6:00pm **SS+AS+EN-TuA12 Crystalline Growth of Ice - Studying the Transition from the First Wetting Layer to Multilayers with Scanning Tunneling Microscopy**, ***Barbara Lechner**, S. Maier, M.B. Salmeron*, Lawrence Berkeley National Laboratory

The growth of water layers on model substrates has been studied intensively, yet many questions still remain [1,2]. After many years of research, the structure of the first wetting layer on metal surfaces has been determined in comprehensive experimental and theoretical studies [3-5]. A surprisingly complex behavior was revealed, showing that the strain caused by the mismatch of the hexagonal planes in the ice crystal structure and the lattice of the substrate is released by forming structures that include rotated hexagons, pentagons and heptagons of molecules, in addition to strongly bound hexagonal rings commensurate with the substrate. A range of experimental and theoretical investigations showed that, on many substrates, the water monolayer does not expose any dangling hydrogen bonds as all water molecules adsorb either flat-lying or with a hydrogen atom pointing towards the surface [1,6]. Growth of multilayer water films that preserve the "down-pointing" average dipole orientation of water has been proposed to occur in some cases, resulting in the formation of "ferroelectric ice" [7]. However, the growth of the entropically more favorable, proton-disordered ice requires flipping some of the molecules in the first layer to expose dangling hydrogen bonds. Such molecular reorientation may be kinetically hindered, and has been invoked to be the reason for the hydrophobic character of many water monolayer films at low temperatures [6].

Here, we present high-resolution scanning tunneling microscopy (STM) measurements of water layers adsorbed on Pt(111) and Ru(0001) to study the transition from the first layer to multilayers. We observe that a second water layer initially grows in an amorphous structure when grown on the crystalline monolayer containing pentagons, hexagons and heptagons of water molecules. To facilitate the growth of ice in a bulk-like hexagonal arrangement, the first wetting layer needs to rearrange into a hexagonal structure commensurate with the surface.

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Surface Science
Room: 112 - Session SS+EN-TuA

Photocatalysis, Photochemistry, and Chirality at Surfaces
Moderator: Arthur Utz, Tufts University

2:20pm **SS+EN-TuA1 Photoemission of Electron from Diamond Into Water: Enabling Novel Electrochemical Reduction Reactions**, ***Robert Hamers***, *D. Zhu, L.H. Zhang,* University of Wisconsin-Madison, *J. Bandy,* University of Wisconsin-Madson, *G.M. Nathanson, J.R. Schmidt*, University of Wisconsin-Madison

Diamond's unusual property of negative electron affinity has long been used to enhance electron emission in vacuum. Recently we have demonstrated that diamond's facile electron emission properties can also be extended to solid-liquid interfaces. Electron photoemitted from diamond into water lead to formation of solvated electrons, widely regarded as the chemist's perfect reducing agent. We demonstrate the inexpensive diamond thin films and diamond powder can be used as solid-state sources of electrons able to induce the reduction of N2 to NH3 and the selective reduction of CO2 to CO. In this talk we will discuss the factors that influence electron emission into liquids, differences from emission into vacuum, and how electrons emitted into liquids can induce novel reduced chemistry not possible with traditional photocatalysts.

2:40pm **SS+EN-TuA2 STM Tip-Induced Desorption of TMAA from TiO_2(110): Model Study of a Photocatalytic Process**, ***Denis Potapenko***, *R.M. Osgood, Jr.*, Columbia University

Titanium oxide is a versatile photocatalytic material with numerous applications in the areas related to utilization of solar energy. Scanning Tunneling Microscopy (STM) allows explorations on the single molecule basis thus providing important insight into the physical phenomena involved in photocatalysis. Our experiments examine the tip-induced chemistry of trimethyl acetic acid (TMAA) molecules adsorbed on TiO_2 rutile(110) surface;this systems was chosen as a model for light-driven catalysis since it is easily imaged with STM and since this system has been the subject of many earlier studies of photo and thermal chemistry. In present work we study the electrical hole-driven desorption of TMAA molecules, initiated by the charges, injected from the STM tip. Different values of the flux and the energy of the excitation charges were achieved by the simultaneous control of the setpoint current and the bias voltage of the STM tunneling junction. The dynamics of the tip-induced desorption of TMAA was compared with the photo-induced dynamics of the same reaction. In the latter experiments the monochromated light from a UV lamp was used as the source of excitation. We show that there is a threshold energy for a hot hole below the edge of the TiO_2 valence band that is required for TMAA photo-desorption.

3:00pm **SS+EN-TuA3 Ultrafast Time-resolved Photoelectron Spectroscopy of Photocatalytic Surfaces**, ***Hrvoje Petek***, *S. Tan, A. Argondizzo*, University of Pittsburgh **INVITED**

We investigate the ultrafast optical excitation and electron relaxation pathways for the clean and molecule covered rutile TiO_2(110) surface. Using high power, broadly tunable (2.9-4.6 eV), 20 fs noncollinear parametric amplifier excitation source, we perform multiphoton photoemission (mPP) spectroscopy of TiO_2 surface. The energy, momentum, and pump-probe delay time resolved mPP spectra provide information on the occupied and unoccupied density of states that participate in photoemission from the valence band or the Ti-3d defect states on reduced TiO_2 surfaces. We find a new bulk transition between the Ti-3d bands of t_{2g} and e_g symmetry, which dominates the photoemission process form the Ti-3d defect states below the conduction band minimum of TiO_2.[1] The 3D mPP spectra provide information on the phase and energy relaxation of photoexcited electrons and holes.[2] Adsorption of molecules introduces adsorbate-induced resonances,[3,4] which can be excited by charge transfer excitation from the Ti-3d defect states. Metal nanoparticles grown on TiO_2 also open new photoemission pathways. We map out the energy and momentum distributions of the adsorbate and nanoparticle resonances as well as their relaxation dynamics.

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2. Cui, X.; Wang, C.; Argondizzo, A.; Garrett-Roe, S.; Gumhalter, B.; Petek, H., Transient excitons at metal surfaces. *Nat Phys*10, 505 (2014).
3. Onda, K.; Li, B.; Zhao, J.; Jordan, K. D.; Yang, J.; Petek, H., Wet Electrons at the H_2O/TiO_2(110) Surface. *Science*308, 1154 (2005).
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4:20pm **SS+EN-TuA7 Surface and Interface Properties of Photoelectrocatalysts for Solar Fuels**, ***Bruce Koel***, *C.X. Kronawitter, P. Zhao, Z. Chen*, Princeton University

Experiments using well-defined model catalysts under controlled conditions and utilizing a range of spectroscopic techniques for characterization of surface and interface properties and the nature and reactivity of surface-bound species can greatly advance understanding of the structure and reactivity of photoelectrocatalysts for solar fuels. We report on several of our recent studies, which include investigations of the effects of dopant incorporation on the structural and chemical properties of the α-Fe_2O_3(0001) surface for water oxidation catalysis, facet-dependent activity and stability of Co_3O_4 nanocrystals towards OER, and the interaction of water with GaP(110), a semiconductor that is known to enable selective CO_2 reduction to methanol in aqueous solutions of CO_2 and nitrogen-containing heteroaromatics. For water oxidation on α-Fe_2O_3, we found that Ni doping in thin films of model catalysts caused a new termination for the films and induced formation of more stable surface-bound OH groups. For the Co_3O_4 system, we used the well-defined morphologies of nanocubes and nanooctahedra to demonstrate that the (111) surfaces vastly out-perform the (100) surfaces for OER activity (overpotential and current density). Finally we have spectroscopically identified *in situ* the surface-bound species on GaP(110) associated with exposure to water using ambient pressure photoelectron spectroscopy (APPES). These observations on model systems afford further analysis and discussion of the role of surface-bound species in mechanisms for catalyzed water oxidation and CO_2 reduction.

4:40pm **SS+EN-TuA8 Improving Hematite-Based Solar Water Splitting by Surface Modification with Sn, Ti, and FeOOH**, ***Anjli Patel***, *A.J. Abel,* Drexel University, *I. Garcia-Torregrosa,* Utrecht University, Netherlands, *B. Opasanont, J.B. Baxter*, Drexel University

Photoelectrochemical (PEC) water splitting with hematite (α-Fe_2O_3) photoanodes presents a promising route to sustainable energy production due to hematite's favorable bandgap, chemical stability, and widespread abundance. However, limitations arise from sluggish oxygen evolution reaction (OER) kinetics at the hematite-electrolyte interface, requiring a significant overpotential to induce photocatalysis. We report on the effects of Sn, Ti, and FeOOH surface treatments on hematite photoanodes to improve PEC performance by overcoming surface kinetic limitations. Thin film hematite photoanodes were fabricated by successive ionic layer adsorption and reaction (SILAR) of FeOOH on F:SnO$_2$–coated glass substrates, followed by annealing at 450 C to induce phase transition of FeOOH into hematite. Subsequent annealing at 775 C caused diffusion of Sn from the F:SnO$_2$ substrate through the hematite, resulting in 0.5at% Sn concentration at the photoanode surface. Current-voltage testing revealed that the presence of Sn in the hematite film significantly reduced the photocurrent onset potential, suggesting improved hole injection efficiency. Electrochemical impedance spectroscopy (EIS) revealed a reduction in the surface state charge transfer resistance ($R_{ct,ss}$) by 2 orders of magnitude, supporting the importance of interfacial kinetics. Hematite photoanodes doped with up to 10% Ti were also prepared by incorporating titanium into the SILAR deposition bath. Ti doping decreased the onset potential by 600 mV and significantly increased the plateau photocurrent density from 0.01 mA/cm^2 at 1.23 V vs. RHE for undoped hematite to nearly 0.6 mA/cm^2 for Ti-doped photoanodes. EIS showed that Ti-doping reduced the $R_{ct,ss}$ at applied potentials ranging from 0.8 to 1.6 V vs. RHE, indicating a possible catalytic effect on the OER reaction at the photoanode surface. FeOOH films were deposited on the hematite photoanodes by an additional SILAR step, which reduced the photocurrent onset potential and increased the plateau photocurrent density by 20%. Unlike Ti, the FeOOH surface treatment exhibited little to no effect on the $R_{ct,ss}$, suggesting that FeOOH does not directly catalyze the OER. However, both the FeOOH treatment and Ti doping significantly increased the peak surface state capacitance, which may be attributed to an increase in density of charged states at the hematite surface, resulting in higher plateau photocurrent. Together, these treatments yield photocurrents that are 3x larger than previous reports using SILAR-deposited planar hematite films, offering promising opportunities to overcome challenges in PEC water splitting with hematite photoanodes.

5:00pm **SS+EN-TuA9 Metalation of a Polypyridine Macrocycle on Au(111): Preparation of a Water Reduction Catalyst on a Solid Substrate**, ***Gerson Mette***, *D. Sutter, S. Schnidrig, B. Probst, R. Alberto, J. Osterwalder*, Universität Zürich, Switzerland

Within the search for new materials and methods for renewable energy resources, photocatalytic water splitting is a very promising field of study. In this framework, a polypyridine macrocycle was investigated which was already described in 1984 but only superficially examined [1]. It shares some similarities to porphyrins but with pyridyl subunits instead of pyrrol, hence the given trivial name: *pyrphyrin*. A high stability of the pyrphyrin and corresponding complexes is indicated due to its conjugation, planarity and cyclic nature. Furthermore, metal complexes based on pyrphyrin show promise as water reduction catalysts.

In this study, we examined the preparation of a pyrphyrin metal complex on a single crystalline surface in ultrahigh vacuum. In a first step, pyrphyrin coverages of approximately one monolayer and less, as determined by XPS measurements, were obtained by sublimation of the molecules on a Au(111) surface at room-temperature. By means of Low-Energy Electron Diffraction (LEED) and Scanning Tunneling Microscopy (STM), two distinct phases depending on the surface coverage were identified and structurally characterized. In a second step, deposition of Co metal at the level of 5% of a monolayer and subsequent annealing led to the formation of an almost complete monolayer of Co-ligated pyrphyrin molecules.

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5:20pm **SS+EN-TuA10 Chiral Selective Chemistry Induced by Natural Selection of Spin-Polarized Electrons by DNA**, ***Richard Rosenberg***, Argonne National Laboratory, *D. Mishra, R. Naaman*, Weizmann Institute of Science, Israel

Most biomolecules can be synthesized in two different mirror-image (chiral) shapes, namely two enantiomers. The enantiomers are recognized by their ability to rotate the polarization of linear polarized light either to the left (L) or to the right (D). In bio-organisms, sugars are always D and amino acids are always L. How this enantiomeric preference originated remains a mystery. Investigations into possible avenues of prebiotic chiral selectivity have been pursued since the time of Pasteur. Many investigations in this area have been devoted to pathways that involve preferential destruction of a particular isomer in an initially racemic (equal quantities of both enantiomers) mixture, through the interactions of chiral particles such as circularly polarized UV radiation or longitudinally spin polarized electrons. It has been shown that low energy (0 – 10 eV) spin polarized secondary electrons, produced by irradiation of a magnetic substrate, can induce chiral-selective chemistry in an adsorbed adlayer.[1] Additional work has demonstrated that organized, double-stranded (ds) DNA, adsorbed on a gold substrate, acts as a natural spin filter for initially unpolarized, low energy (0 – 1.2 eV) electrons produced by UV irradiation of the substrate, resulting in net polarizations as high as 60%.[2] Experiment and theory indicates that this spin filtering effect should be effective for higher energy (E < 15 eV) electrons as well.[3] In the present study, we probe if low energy secondary electrons, produced by x-ray irradiation of a gold substrate, and transferred through the chiral monolayer, induce enantiomeric selective chemistry in an adsorbed adlayer. To test this, (R)- or (S)-epichloroydrin (C_3H_5ClO, Epi) was adsorbed on a self-assembled monolayer of 70 base pair long dsDNA. The secondary electron-induced reaction was monitored by following changes in the Cl 2p x-ray photoelectron spectroscopy spectra. By kinetic modeling of the reaction, quantum yields (QYs) were determined. For S-Epi the QY was ~16 % greater than for the (R) enantiomer, while the QYs were the same for the two enantiomers when they were adsorbed on bare Au.

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5:40pm **SS+EN-TuA11 Creating Enantioselective Surfaces; Templating and One-to-one Interactions**, ***Wilfred Tysoe***, University of Wisconsin-Milwaukee

The mode of operation of heterogeneous chiral modifiers can be classified into those operating as templates, where several modifier molecules act in concert to define a chiral adsorption site, or one-to-one modifiers that form a docking complex between the modifier and a prochiral reactant.

Enantioselectivity is measured by adsorbing chiral probe molecules onto chirally modified surfaces. Templating is illustrated using aminoacids on Pd(111). Scanning tunneling microscopy (STM) reveals that some aminoacids form tetrameric units, and others form dimers. Only those aminoacids that form tetramers are enantioselective implying that the tetramers act as templates.

Naphthylethylamine (NEA) is proposed to acts as a one-to-one modifier. The interaction between NEA and a prochiral reactant, methyl pyruvate, is explored using STM. Possible docking complexes are identified using density functional theory and the simulated images are compared with experimental images. Finally, it is shown the tartaric acid on Pd(111) acts as a one-to-one modifier for glycidol and is controlled by hydrogen-bonding interactions.

6:00pm **SS+EN-TuA12 Single-Molecule and Single-Active-Site Studies of Stereocontrol by Chemisorbed Chiral Molecules**, ***Peter McBreen***, *Y. Dong, J.C. Lemay, G. Goubert,* Laval University, Canada, *M.N. Groves, B. Hammer*, Aarhus University, Denmark

Isolated adsorbed chiral molecules can stereodirect prochiral co-adsorbates on reactive metal surfaces and the application of this phenomenon underpins a method to perform asymmetric heterogeneous catalytic reactions. Typically, the stereochemical action is attributed to intermolecular interactions in complexes formed by docking the prochiral substrate in a chiral pocket created by the chemisorbed chiral molecule. We will present results from combined variable temperature STM and optB88-vdW DFT studies of individual bimolecular docking complexes formed by enantiopure 1-(1-naphthyl)ethylamine and selected prochiral molecules on Pt(111). The experiments reveal sub-molecularly resolved and time-resolved site-specific and stereospecific data. The results show that a single chemisorbed enanantiomer simultaneously presents several chiral pockets, each displaying a specific prochiral ratio for a given substrate molecule. A hierarchy of metal-molecule and molecule-molecule interactions is found to control prochiral selection at each site. Time-lapsed STM measurements of individual substrate molecules sampling a set of chiral pockets provide new insight on the dynamics of stereocontrol.

Thin Film
Room: 111 - Session TF-TuA

ALD for Emerging Applications
Moderator: Robert Grubbs, Micron Technology, Erwin Kessels, Eindhoven University of Technology, Netherlands

2:20pm **TF-TuA1 ALD ZnO for Rapid Synthesis of Cu-BTC MOF Thin Films and Patterns**, ***Junjie Zhao****, *W.T. Nunn, P.C. Lemaire, Y. Lin, M.D. Dickey,* North Carolina State University, *G.W. Peterson,* Edgewood Chemical Biological Center, *M.D. Losego,* Georgia Institute of Technology, *G.N. Parsons*, North Carolina State University

Metal-organic frameworks (MOFs) are crystalline porous materials that consist of metal ions/clusters and organic linkers. MOFs typically exhibit high surface area, good adsorption capacity and opportunity for post-synthetic modification. However, the insoluble MOF powders typically synthesized through conventional solvothermal methods may not be the ideal configuration for gas filters, chemical sensors and smart membranes etc. Growing MOF thin films onto various functional substrates, especially in a high-throughput process with low energy input, is therefore highly desired for MOF industrial implementation and new applications.

Here we report a rapid room-temperature synthesis route for Cu-BTC ($Cu_3(BTC)_2$) MOF thin films using ZnO nucleation layers deposited via atomic layer deposition (ALD). We find in just 1 minute of exposure to the Cu-BTC precursor solution, dense Cu-BTC thin films can be integrated onto various ALD ZnO coated substrates including silicon wafers, polymer spheres, and fibrous materials. MOF patterns can also be obtained on pre-patterned ZnO surfaces. The space-time-yield of the Cu-BTC production reaches up to $2.9\times10^{4}\ \mathrm{kg\cdot m^{-3}\cdot d^{-1}}$, which is over 10× higher than previous reports. We further investigated the surface reactions between ALD ZnO and MOF precursor solutions using high-resolution EDX, XRD and FTIR. The results suggest hydroxyl double salt ($(Zn,Cu)(OH)_3NO_3$) is an important intermediate to drive the rapid formation of Cu-BTC thin films. Breakthrough tests were performed to demonstrate the high adsorption capacity of these MOF-functionalized materials for toxic industrial chemicals. This rapid room-temperature approach is also promising for new MOF-based composite materials for membrane separation, gas storage, chemical sensing and other applications.

2:40pm **TF-TuA2 Reactions During Atomic Layer Deposition on and in UiO-66-NH_2 Metal Organic Framework Crystals**, ***Paul Lemaire***, *J. Zhao, C. Oldham, G.N. Parsons*, North Carolina State University

Metal organic frameworks (MOFs) are microporous materials with chemically functionalized high surface areas. MOFs are attractive for multiple applications including filtration, gas storage, and catalysis. Post-synthetic modification (PSM) is a way to impart additional functionality into these materials and most PSM techniques reported are solution based processes. Vapor-phase PSM methods are highly desired due to the advantageous efficiency in reagent and solvent reagent removal.

In this work we report on a fundamental study on the functionalization of the UiO-66-NH_2 MOF through atomic layer deposition (ALD). ALD is a vapor phase self-limiting process that enables the controlled deposition of thin films. The UiO-66-NH_2 MOF is of particular interest for its high thermal and chemical stability and catalytic activity. We investigated how UiO-66-NH_2 interact with ALD precursors, including titanium tetrachloride ($TiCl_4$), titanium isopropoxide (TTIP), and trimthylaluminum (TMA).

QCM analysis shows that the UiO-66-NH_2 consumes a relatively large amount of precursor in the first exposure, with a ~16% and ~20% for $TiCl_4$/TTIP and TMA respectively. It is likely that the majority of the MOF pore volume is filled within the first cycle. For the first ALD cycle, purge time ranging 0.5-2.5 hours are necessary to completely remove excess unreacted precursor and byproducts. Following the first cycle, the mass loading per cycle decreases and becomes relatively linear.

In-situ FTIR analysis of the ALD functionalization of UiO-66-NH_2 at 150°C shows that the MOF structure is maintained during the ALD process. Dosing each of the ALD precursors results in a loss of the hydroxyl bands at ~3650, 735, and 675 cm^{-1}, but also a loss of the asymmetric and symmetric carboxylate stretching bands at ~1565 and 1375 cm^{-1} respectively. Upon water exposure, these bands reappear. These changes in the carboxylate stretching bands was consistent with shifting between the hydroxylated and non-hydroxylated UiO-66-NH_2 structure. Finally, the dehydroxylated UiO-66-NH_2 at 250°C was significantly less reactive towards the ALD precursors, suggesting that hydroxyl sites in UiO-66-NH_2 play a large role in ALD functionalization of the MOF. The ability to deposit metal oxide thin films or nanoparticles within UiO-66-NH_2 pores could help improve the MOF catalytic activity.

3:00pm **TF-TuA3 Selective ALD Growth of Pd@Pt Core Shell Nanoparticles and its Application in PROX Reactions**, *K. Cao, Q.Q. Zhu, B. Shan,* State Key Laboratory of Material Processing and Die & Mould Technology, China, ***Rong Chen***, State Key Laboratory of Digital Manufacturing Equipment and Technology, China

Bimetallic nanoparticles (NPs) have attracted great attention due to their unique properties for catalytic applications. Compared with the physical mixture of monometallic NPs or the alloyed bimetallic NPs, the formation of core shell NPs could further enhance the activity, selectivity and stability. The enhanced properties of core shell structure may originate from the lattice strain, bonding interaction and electron transfer due to the core shell interface. Synthesizing core shell nanoparticles (NPs) with well controlled shell thickness and composition is of great importance in optimizing their reactivity.

Here we report the successful synthesis of core shell NPs using an area-selective ALD technique. The selective ALD approach utilizes pinholes on the unsaturated ODTS SAMs layer to achieve selective core shell structure growth. The size, shell thickness, and composition of the NPs can be precisely controlled by varying the ALD cycles. The catalytic performance of Pd@Pt core shell NPs with different Pt shell thickness have been tested towards preferential oxidation of CO under excess H_2 (PROX) reaction. The results show that the core shell structured NPs exhibit both great selectivity and enhanced activity. Core shell NPs with a completely covered monolayer of Pt shell shows optimized selectivity and activity. Density functional theory simulations have been carried out to explain such behavior of the core shell NPs system towards PROX reactions.

3:20pm **TF-TuA4 Thermal and Plasma ALD on Semiconductor Nanowires**, ***Lachlan Black***, Eindhoven University of Technology, Netherlands, *M.A. Verheijen, A.J. Standing, E.P.A.M. Bakkers,* Eindhoven University of Technology, *W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

Semiconductor nanowires represent a novel class of materials structure with a number of interesting properties that give them potential applications in optoelectronic devices, including light-emitting diodes (LEDs), photoelectrochemical systems, and solar cells. Because of the unusually high surface-to-volume ratio of nanowires, the electrical performance of nanowire devices is especially sensitive to the condition of the semiconductor surface. It is well known that the application of thin-film dielectric and conductive layers to semiconductor surfaces can be an effective means of controlling surface properties. Such layers can provide chemical and electrical passivation, functionalisation, and contacting of semiconductor device surfaces. However, most conventional thin-film deposition techniques face severe challenges when confronted by the high-aspect-ratio features represented by nanowire geometry.

Atomic layer deposition (ALD), on the other hand, is ideally suited to thin film deposition on small-dimensioned, high-aspect-ratio structures due to its uniquely self-limiting nature, which results in outstanding uniformity and conformality, and thickness control on the sub-nm level. The application of thin films deposited by ALD to nanowire devices, in order to improve device properties, has previously been reported by a number of authors. However, there has been relatively little effort to systematically study the ALD process on nanowire surfaces in its own right. Nanowires represent an interesting test platform with which to study ALD processes and thin film properties because of the relative ease with which they can be characterised by transmission electron microscopy (TEM).

In this paper we present a fundamental experimental study of ALD on semiconductor nanowires. ALD thin films of various dielectric and conductive materials, including Al_2O_3, TiO_2, ZnO, and HfO_2, are deposited on Si and III-V semiconductor (GaP and InP) nanowire arrays grown by the vapour-liquid-solid (VLS) mechanism, and characterised by high-resolution TEM. Film thickness measured as a function of the number of deposition cycles is used to determine the linearity of the deposition rate and the growth-per-cycle, and these values are compared to those measured on co-deposited planar samples using in-situ and ex-situ ellipsometry. It is shown that both thermal and plasma-assisted ALD processes are capable of depositing films with excellent conformality and thickness uniformity along the length of the nanowires, although differences are observed for different materials. Moreover, TEM images reveal the presence of clearly defined interfacial layers in some samples.

*** TFD James Harper Award Finalist**

5:00pm **TF-TuA9 Capacitive Deionization for Water Desalination Using Charge Storage in Manganese Oxide Films Grown by Atomic Layer Deposition**, ***Jasmine Wallas***, *M.J. Young, C.B. Musgrave, S.M. George*, University of Colorado, Boulder

Capacitive deionization (CDI) is a promising water desalination technique based on the reversible electrosorption of anions (Cl^-) and cations (Na^+). Traditional CDI relies on ion storage in the electric double layer (EDL) on the surface of carbon electrodes. Additional ion storage can be achieved through charge storage in thin films of various materials, such as manganese oxide, that are deposited on the electrodes. In this work, we have demonstrated a dramatic improvement in reversible Na^+ ion storage using MnO_2 films on electrodes prepared using atomic layer deposition (ALD).

The MnO_2 films were prepared by first growing MnO ALD films using bis(ethylcyclopentadienyl) manganese and H_2O on flat Ti electrodes. These MnO films were then electrochemically oxidized to MnO_2. Conversion of MnO to MnO_2 was monitored during electrochemical oxidation with cyclic voltammetry. A large increase in capacitance occurred concurrently with the conversion to MnO_2. The reversible adsorption of Na^+ under applied potential in NaCl solutions was then confirmed with electrochemical quartz crystal microbalance (E-QCM) analysis. Adsorption of Na^+ and an elemental composition of $Na_{0.25}MnO_2$ after Na^+ adsorption was further verified with x-ray photoelectron spectroscopy (XPS) studies.

MnO_2 films on flat Ti electrodes dramatically increased the ion storage from NaCl solutions. A maximum areal capacitance of 5.6 mF/cm^2 was observed from MnO_2 films prepared from MnO ALD films with an initial thickness of 447 Å. This areal capacitance is >170 times larger than the areal capacitance of an uncoated Ti electrode. MnO_2 films were also prepared on electrodes composed of high surface area carbon nanotubes (CNTs) using 200 cycles of MnO ALD and electrochemical oxidation. These MnO_2-coated CNT electrodes also displayed a significant increase in areal capacitance compared with uncoated CNT electrodes. These results indicate that MnO_2 coatings on electrodes could substantially enhance the charge storage for CDI and water desalination.

5:20pm **TF-TuA10 Magnetoelectric Effect in Multiferroic Nanocomposites of Atomic Layer Deposition $Pb(Zr,Ti)O_3$ Coupled with Templated Mesoporous $CoFe_2O_4$**, ***Diana Chien***, *A. Buditama, L. Schelhas, S.H. Tolbert, J.P. Chang*, University of California at Los Angeles

Ultra-thin, uniform, and conformal PZT films are needed to engineer nanoscale multiferroic composites with complex architectures. By coupling the piezoelectric PZT film with a magnetostrictive material (e.g. CFO), a magnetization (polarization) can be induced by an applied electric (magnetic) field via the strain-mediated magnetoelectric coupling effect, in which strain is transferred at the interface between the piezoelectric and magnetostrictive layers. 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 provides superior uniformity and conformality over complex surface structures with high aspect ratios.

ALD PZT thin films were synthesized by depositing alternating layers of PbO, ZrO_2, and TiO_2 layers using $Pb(TMHD)_2$, $Zr(TMHD)_4$, and $Ti(O^{\cdot}i\text{-}Pr)_2(TMHD)_2$ as metal precursors and H_2O as the oxidant. The number of local cycles and global cycles were regulated to achieve the desired stoichiometry and thickness, respectively. ALD of PZT was studied to obtain (100) oriented $Pb(Zr_{0.52}Ti_{0.48})O_3$ on Pt (111) oriented silicon substrates. In order to attain a highly oriented PZT thin film, a (100) textured $PbTiO_3$ seed layer was required because PZT orientation is generally governed by nucleation. The stoichiometry and crystallinity of PZT films were confirmed by XPS and XRD measurements. The conformality was confirmed over high aspect ratio structures.

By controlling the composition, thickness, and conformality of ALD PZT thin films, multiferroic nanocomposites were engineered. Specifically, ALD PZT thin films were shown to uniformly coat the walls of nanoscale templated mesoporous CFO (with neck size of 6 nm in radius) to form a complex 0D-3D nanocomposite. XPS and XRD measurements confirmed the elemental analysis and crystallinity, respectively, of the PZT/CFO nanocomposites. To study the magnetoelectric coupling effect, the nanostructure was electrically poled ex-situ and the resulting magnetic moment was measured via SQUID while sweeping in-plane and out-of-plane magnetic fields. The in-plane results show that there is no change in magnetization as a function of voltage, which is due to the effect of substrate clamping. The out-of-plane results show that the magnetization changes as a function of voltage. The mesoporous CFO coated with 3 nm thick PZT film shows a greater magnetization change than the 6 nm thick PZT film, suggesting that porosity in the templated mesoporous CFO matrix is needed for a greater magnetoelectric coupling effect.

5:40pm **TF-TuA11 Ultralow Density Metal Oxide Foams by Atomic Layer Deposition on Sacrificial Carbon Nanotube Matrices**, ***Jesse Jur***, *K.L. Stano, P.D. Bradford*, North Carolina State University

Ultralow density materials ($\rho \leq 10$ mg cm^{-3}) have recently gained widespread attention, and have been realized in many forms including silica, and carbon-based aerogels, as well as engineered structures such as inorganic micro- and nanolattices. Porous metal oxides, particularly alumina, are desirable due to their semiconducting and dielectric properties as well as thermal, mechanical, and chemical stability. Historically, monolithic alumina aerogels have been fabricated using sol-gel processes. Although this and other self-assembly methods can produce very high surface area aerogels, they have a moderate low density ($\geq$ 30 mg cm^{-3}), and little to no control over pore size and structure. We present here a method by which aligned CNTFs are used as unique sacrificial templates for the formation of anisotropic, large-scale inorganic nanotube architectures that exhibit the combined characteristics of high surface area, ultralow density, and mechanical robustness. Using ALD, conformal coatings were deposited onto the CNTFs, followed by their removal via calcination in air to leave behind an interconnected network of thin-walled and aligned nanotubes of the ALD metal oxide. Analysis shows that the use of alumina ALD, one can achieve a density as low as 1.2 mg cm^3, 16x lower than previously report alumina foams. Furthermore, both CNT/alumina hybrid foams and pure alumina nanotube foams exhibit unprecedented elastic recovery following 50% compression, and possess values for strength and Young's moduli which exceed those of aerogels with similar densities. The scaling behavior of Young's modulus to foam density for pure alumina foams exhibits a power-law dependence of $n \approx 1.9$, attributed to superb ligament connectivity. As a low thermal conductivity insulation, a foam of 1 cm thickness is demonstrated to reduce a flame temperature of 1000 ° C to 45 ° C after 5 min of direct flame contact.

6:00pm **TF-TuA12 The Structure and Optical Properties of ALD $W{:}Al_2O_3$ Nanocomposite Films**, ***Shaista Babar***, *A. Mane,* Argonne National Laboratory*, A. O'Mahony,* Incom, Inc.*, A. Yanguas-Gil, J. W. Elam*, Argonne National Laboratory

A highly robust $W{:}Al_2O_3$ nanocomposite material has been reported by ALD method and used in microchannel plates (MCPs) and MEMS devices [1,2]. By adjusting the W cycle percentage during the nanocomposite synthesis, the resistivity can be tuned in the range of $10^{12} - 10^{8}\ \Omega$. Here we report a systematic study of the structure and optical properties of ALD deposited nanocomposite $W{:}Al_2O_3$ films using SEM, TEM, XRD, XRR, XPS, ellipsometry and UV-vis-IR spectroscopy. General oscillator and Kramers-Kronig consistent B-spline models were used to extract the optical constants of the films. We studied the impact of the composition and microstructure on the optical properties of $W{:}Al_2O_3$ layers as ALD cycle ratio and metal contents. We report a systematic decrease in the bandgap associated with the increase in the W content. We also discuss the high thermal stability and high absorptivity of W:Al2O3 and propose it as an ideal candidate for concentrated solar power receivers .

References:

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Vacuum Technology
Room: 230B - Session VT-TuA

Gas Dynamics and Modeling, Pumping and Outgassing
Moderator: Marcy Stutzman, Jefferson Lab, Jacob Ricker, NIST

2:20pm **VT-TuA1 The Evolution of Cryopumps**, ***Sergei Syssoev***, Brooks Automation **INVITED**

Cryopumping is a widely used technique to produce vacuum in an enclosed space via removal of residual gases by cooling them to the point that they are condensed or adsorbed on an appropriate cryogenic surface. Depending upon the application and the gas species, cryopumps operate at different temperatures between 4K and 150K. To attain these temperatures, different thermodynamic cycles are employed ranging from helium liquefaction to mixed gas auto-cascaded systems. Of these various thermodynamic cycles the Gifford-McMahon (GM) cycle has emerged as the dominant cycle for economically delivering the appropriate cooling power at the appropriate temperatures required for cryopumping. Cryopumps based on GM cryocoolers have been commercially adapted to a variety of vacuum processes; notably semiconductor substrate processing equipment, flat panel display fabrication, thin film coatings, analytical instruments and space simulation systems. Built around a dual stage cryocooler, GM cryopumps consists of two internal cryocondensation regions (arrays) that operate at different temperatures. The warmer (first) stage is generally operated at temperatures between 65K and 100K, condensing mainly residual water vapor and other type I gases such as hydrocarbons, carbon dioxide etc. The colder (second) stage is kept at 8K to 20K, which allows condensing of type II gases (such as nitrogen, argon, oxygen) and adsorbing type III gases (hydrogen, helium, neon). To adapt a cryogenic pump to a specific application the geometry and temperatures of the condensing arrays can be modified or tuned to suit the user's application.

By far the dominant application of cryopumping is for the semiconductor fabrication processes of physical vapor deposition (PVD) and ion implantation. There are significant differences in the vacuum environments, namely the gas species and gas densities in which these two processes are conducted. Over time, the vacuum requirements of these processes have become more stringent as line widths decreased in keeping with Moore's Law. In response to the changing vacuum requirements for these processes, the designs of closed cycle cryopumps have evolved. The evolutionary performance improvements of GM cryopump that has taken place in the past few decades will be discussed in this work. Extensive developments have led to significant increase of storage capacity (up to factor 5), pumping speed, pressure dynamics, functionality and energy efficiency. The safety aspects of cryopumping of explosive gases such as oxygen (ozone) and hydrogen will also be discussed.

3:00pm **VT-TuA3 Simulation of a Large Linear Jet Mercury Diffusion Pump with the Test Particle Monte Carlo Method**

Xueli Luo, *T. Giegerich, C. Day*, Karlsruhe Institute of Technology (KIT), Germany

In current nuclear fusion research, the cryopump in various designs has become the standard solution for pumping the plasma chamber. However, considerable amounts of accumulated tritium have been found the issues towards a fusion demonstration power plant (DEMO). A recent study has shown that the mercury diffusion pump has the potential to replace the cryopump, and KIT has been charged to develop a new linear mercury diffusion pump [1]. Obviously, a reliable simulation tool is essential in such a development.

The first mercury diffusion pump was invented by W. Gaede 100 years ago. In the fifties of last century, a large, linear mercury diffusion pump was built and tested in Livermore Research Laboratory [2]. In this paper, we will present the simulation of this pump by ProVac3D, which is a versatile Test Particle Monte Carlo simulation code developed by KIT [3-4]. Based on the fact that the profiles of the mercury jets are hardly changed by the gas load, the simulation was carried out in two steps. First, the background density of the mercury molecules established by the mercury jets was calculated. Secondly, the collision between the molecules of the gas load (N_2 at 15°C) and the mercury molecules had been considered. In order to achieve high simulation precision, ProVac3D had been parallelized, and 10^{12} test molecules were simulated at a supercomputer. The calculated pumping probability, which is the ratio of the number of particles absorbed at the pump bottom to the number of the total simulated particles, was compared with the ratio without collisions between the gas load and the mercury jets. In this way, the pumping effect of the mercury gas jet had been clearly revealed and compared with the experimental data. The agreement is good and this novel simulation approach with ProVac3D will be employed in the development of such a pump for DEMO. Further investigation to combine the Monte Carlo simulation of the gas load with the CFD calculation of the mercury jet is in plan.

References

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3:20pm **VT-TuA4 Monte-Carlo and Angular Coefficients Simulations of Complex Vacuum Systems Equipped with NEG Pumps**

Fabrizio Siviero, *T. Porcelli, G. Bongiorno, M. Urbano, E. Maccallini, P. Manini*, SAES Getters, Italy

The use of analytical and numerical tools for the simulation of several physical quantities in complex vacuum systems is becoming a well-established practice. Applications range from large machines like particle accelerators to smaller systems, for example analytical instrumentation or special processing chambers. The computational approach is essential whenever an accurate estimation of pressure profiles or effective pumping speeds is needed for vacuum systems that do not present a very simple geometry. This is very often the case of real UHV systems, where NEG pumps are increasingly employed to improve the performances of the pumping system in terms of base pressure, size, weight or power consumption.

Two main approaches are currently used in the field, i.e. the test-particle Monte Carlo (TPMC) and the Angular Coefficients (AC) methods. At SAES labs both these methods are being used, the former by means of the MOLFLOW+ code, the latter with an interface developed internally in MATLAB and ANSYS environment. The simulation work has two main aims: first as a tool to support the development of NEG products, then more and more frequently to help customers in taking full advantage of the use of getter technology in their systems. Indeed, the use of NEG pumps in the vacuum layout may allow redesigning the complete system, for example enabling the improvement of other important parts in the design of the machine.

The case of NEG pumps simulation presents some peculiar features, since it is not always possible to model the pump as a simple absorbing surface, i.e. the flange inlet, but the complete device must be modelled. Thus it becomes important to properly set the characteristics of the pumping surface in terms of geometry and sticking probability. Some examples will be presented about:

i) the NEG characterization in terms of pumping speed for different gases;

ii) the design of new systems and the upgrade of existing facilities, where NEG pumps, including combination pumps (NEXTorr®) and custom solutions, are used to improve the vacuum level or solve practical issues related to the size and weight of the conventional pumping system.

Results show that vacuum modeling of NEG pumps is an helpful tool to system design and optimization.

4:20pm **VT-TuA7 Simulation of Steady-State and Impulse Pressure Profiles in Front-End of A1-Beamline at Cornell High Energy Synchrotron Source**

Yulin Li, Cornell University

During summer 2014 accelerator shutdown, a pair of Cornell Compact Undulators (CCUs) was installed at Cornell Electron Storage Ring (CESR), together with a 3.5-long vacuum chamber with 5-mm vertical aperture. In a canted arrangement, these CCUs provide much brighter X-ray beams to 5 (out of 12) user stations at Cornell High Energy Synchrotron Source (CHESS). To take full advantage of the brighter sources, one of CHESS beamline, namely A1 beamline, was re-designed entirely and constructed with new vacuum chambers along ~25-m length. Similar to most 3rd generation light sources, the new CHESS A1 beamline deployed a windowless design without any vacuum barrier between CESR and A1 user station. However, the windowless design poses potential risks to CESR ultra-high vacuum (UHV) systems from potential vacuum excursions at the user station. Differential pumping and various protection interlocks are incorporated in the A1 beamline to mitigate the risks. In this paper, vacuum responses to large gas loads in A1 beamline front-end section were simulated using a test-particle Monte-Carlo program, MolFlow$^+$ [1]. The front-end sector of the A1 beamline is constructed of UHV-compatible components with all-metal seals, including an X-ray optics box, beam shutters, two collimators, and all-metal gate valves etc. Vacuum pumping consists of a large turbo-molecular pump (1300 l/s) at the mirror box, and 6 additional sputtering-ion pumps (SIPs) and non-evaporable getters (NEGs) with pumping speed ranging from 45 to 200 l/s. To simulate vacuum incidents, a very large gas load (0.1 torr×liter/sec) is introduced at the X-ray optics box. The vacuum pressure profiles are simulated along the front-end sector to assess the impact of the large gas load to CESR UHV system, for various pumping conditions. To evaluate the A1 front-end sector as a vacuum delay-line, time-dependent pressure profiles are also simulated with MolFlow$^+$. The simulation results indicate that CESR UHV system is immune from vacuum incidents at CHESS user stations and the A1 front-end sector acts as effective delay line.

This work is supported by the National Science Foundation, under Grant# DMR-1332208 and 0936384. Mr. Aaron Lyndaker of CHESS provided a 3D model of A1 front-end used in the simulations.

[1] MolFlow$^+$ is available from CERN's web-site: http://test-molflow.web.cern.ch/

4:40pm **VT-TuA8 APS-Upgrade Storage Ring Vacuum System Design using SynRad/MolFlow+ with Photon Scattering**, ***Jason Carter***, Argonne National Laboratory

The SynRad/MolFlow+ vacuum simulation package from CERN has been used to evaluate a conceptual design of a storage ring vacuum system for the APS-Upgrade project. The design requirements call for a system that can reach sufficiently low pressures within a reasonable commissioning time in order to achieve required beam lifetimes. A SynRad/MolFlow+ simulation of the storage ring vacuum system pressures has been computed which includes photon scattering and predicts photon stimulated desorption outgassing rates from the irradiated vacuum surfaces. The vacuum system design incorporates two important analyses. Synchrotron radiation absorbers are located at critical lattice sites in order to both mitigate high heat loads and to localize the high predicted gas loads so that they can be efficiently removed with discrete pumps. In addition, the residual gas species are calculated to identify regions with high molecular gas concentrations. Vacuum pumping is then designed to mitigate the high mass gas loads and increase beam lifetimes.

5:00pm **VT-TuA9 Simulation and Measurement of Radioactive Radon in the KATRIN Main Spectrometer**, ***Joachim Wolf***, Karlsruhe Institut for Technology (KIT), Germany

The objective of the **Ka**rlsruhe **Tri**tium **N**eutrino experiment (KATRIN) at the Karlsruhe Institute of Technology (KIT) is the measurement of the electron neutrino mass. A central component is the Main Spectrometer (MS), where the energy of the β-electrons from tritium decay (18.6 keV) will be measured with high precision. It consists of a large ultra-high-vacuum vessel with a volume of 1240 m^3. The pumping system of the MS consists of turbo-molecular pumps, a large-scale getter pump (3000 m NEG strips, St707) and three cryo-baffles at LN_2 temperature, designed to maintain an ultimate pressure in the range of 10^{-11} mbar.

The NEG strips, as well as the stainless steel walls are known to emanate small amounts of radon atoms, increasing the intrinsic background rate, which would limit the sensitivity for the neutrino mass. The cryogenic copper baffles are expected to capture most of the radon, before it decays in the main volume. However, radon does no not stick to the cold surface indefinitely. There are two possibilities, it either desorbs after a limited residence time (depends on desorption enthalpy and baffle temperature), or it decays into polonium. In the first case, it can contribute again to the background rate.

This work reports on radon measurements with cold baffles at various temperatures and compares the results with Test-Particle Monte-Carlo (TPMC) simulations. The simulation was performed with a modified MOLFLOW+ code, where we added two new, time-dependent features, (i) a finite residence time for all adsorbing surfaces, and (ii) the half-life of the test particles. For the measurements we used two different radon isotopes with a half-life of 4 s and 56 s, respectively. By comparing measured rates with TPMC simulations for different residence times, we want to learn more about the surface conditions of the baffles (Cu, Cu_2O, H_2O) and the corresponding desorption enthalpies.

This work has been supported by the German BMBF (05A14VK2).

5:20pm **VT-TuA10 Degassing of the Kicker Magnet in J-PARC RCS via New *In Situ* Baking Method**, ***Junichiro Kamiya***, *N. Ogiwara, M. Kinsho*, Japan Atomic Energy Agency

The usual way to reduce outgassing from a device in vacuum is to heat up a whole vacuum chamber containing the device. However, the situation, where this method can be applied, is limited due to the heat expansion of the chamber. Especially in accelerators, where the vacuum chambers are connected with nearby beam pipes, this normal bake-out method may not be applied. If a heat source and heat shields are appropriately installed inside the chamber, heat flux is directed to the device. Therefore the device can be baked out without raising the temperature of the vacuum chamber.

One candidate for such bake-out method to be applied is kicker magnets in J-PARC 3GeV synchrotron (RCS), which are installed in large vacuum chambers. The kicker magnets are installed in vacuum to prevent the discharge by high voltage. The kicker magnet mainly consists of Ni-Zn ferrite cores, aluminium electrode plates. The total outgassing rate of the materials is large due to the large surface area. Therefore it is very important to develop a degassing method for the kicker magnets in the beam line because the vacuum quality may become poor after repeated exposures to air for the maintenances. The main outgassing component of those kicker magnet components is water vapour. Therefore the bake-out temperature should be above 100 °C, which is the typical desorption temperature of water vapour from the general surface. In the RCS beam line, 3 and 5 kicker magnets are located in vacuum chambers, whose length is 3 and 5 m, respectively. It is undesirable to use a normal baking method like baking the vacuum chamber of the kicker magnets because the large heat expansion of the vacuum chamber will break nearby equipment such as alumina ceramics pipes. By applying the bake-out method, which is mentioned at the beginning, only the kicker magnet is heated without raising the temperature of the vacuum chamber. In the first stage, we performed the operability assessment of the new degassing method by the calculation with a simple model and the principal experiments using the kicker magnet, which have the same structure as the production kicker magnets in RCS. As a result, the kicker components were heated up above 100 °C by a wide margin, while keeping the temperature rise of the vacuum chamber less than 20 °C. Next, we developed the design of the heater, which has a good maintainability. The small heater of graphite, which is installed through a maintenance port of the vacuum chamber, is designed. The ideal temperature distribution was obtained with this graphite heater. Furthermore, the outgassing of the graphite was suppressed by the heating process.

5:40pm **VT-TuA11 Uncertainty of UHV Flowmeter Standard Related to the Gas-Surface Interaction**, ***Felix Sharipov***, *Y.B. Barreto*, Universidade Federal do Parana, Brazil

Gas flows through orifices of various shapes are used in the primary metrology of vacuum in order to develop a primary standard of conductance [1]. Since the orifices are usually very think and the most part of gaseous molecules passes through the orifice without a collision with its surface, it is assumed the diffuse scattering for those particles which undergo collisions with the surface. However, many experiments, see e.g. [2], pointed out a significant deviation from the diffuse scattering especially for light gases like helium so that the conductance calculated on the basis of the diffuse scattering can be different from the real one and that leads to an additional uncertainty that is not included in the total uncertainty [1]. As was pointed out in Ref.[3], the diffuse-specular model of the gas surface interaction having just one adjustable parameter contradicts to some experimental data on the so-called thermomolecular pressure difference. At the same time, the Cercignani-Lampis (CL) model containing two adjustable parameters describes more physically the gas-surface interaction. The aim of the present work is to calculate the conductance of orifices used in the primary metrology based on the CL model using the accommodation coefficient extracted from various experimental data. A comparison of these data with those obtained for the diffuse scattering will give us the uncertainty related to the gas-surface interaction. Preliminary results show that the uncertainty is within 1%. Basing on these data, some recommendations to reduce the uncertainty will be given.

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6:00pm **VT-TuA12 Investigation of the use of Viton as Certified Reference Material for Outgassing**, ***Janez Setina***, Institute of Metals and Technology(IMT), Slovenia

Goal of this study was to make samples with well known outgassing rate which can be used as a reference for calibration and validation of different outgassing measurement facilities.

Main criteria for selection of suitable material were (i) sufficient solubility of different gases in the material (ii) diffusion constant for different gasses in the range from 10^{-8} cm^2/s to 10^{-6} cm^2/s, and (iii) material shall be "clean" and compatible with high vacuum, which means it shall not release volatile organic compounds. Only materials which have sufficient repeatability and reversibility of gas absorption could be used as reference samples. Materials with desired properties can be found among polymers and we selected Viton (FPM-fluoropolymer) as a good candidate for outgassing reference samples. Use of Viton in high vacuum systems down to 10^{-7} Pa is well established.

We have prepared outgassing reference samples in the following way: pieces of Viton were placed in a gas loading cell and were evacuated on an ultrahigh vacuum system for sufficiently long period to get fully degassed state. Then the loading cell was filled with a pure gas or gas mixture at a pressure up to several 100 kPa and the samples were kept in the gas for several days to penetrate into material to a fully saturated state. Samples were removed out of the loading cell just before they were placed into the outgassing rate measurement apparatus.

A reference sample can be first loaded with a certain gas or gas mixture and measured by a "primary" outgassing measurement system (like the system in PTB-Germany which was developed in the frame of EMRP-IND12 project), yielding a certified reference value of the outgasing rate as a function of time. Then the same sample can be re-loaded with the same gas and under the same conditions and sent in the loading cell to a user in industry or another laboratory for the measurement in their system.

Certified reference samples can be used in round robin tests for the proficiency testing of systems in different laboratories. Distinctive feature of newly developed reference samples based on Viton material is that they can be reloaded many times and with many gases, and also with mixtures of gases at arbitrary concentration ratios. Gases which do not react chemically with Viton are expected to produce reproducible outgassing rates. This was confirmed in our tests with gases H_2, He, Ar, Kr, CH_4, N_2, O_2 and CO.

Support through the EMRP IND12 project is gratefully acknowledged. The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union.

Biomaterial Interfaces
Room: Hall 3 - Session BI-TuP

Biomaterial Interfaces Poster Session

BI-TuP1 Flash Networking Poster: Simple Method Toward Lignin Based Surface Coatings

Patrick Burch, *P.B. Messersmith*, University of California at Berkeley

Lignin is the second most abundant biopolymer on earth. Millions of tons are produced annually as a byproduct of the paper industry but yet its use is limited to mostly low-value applications, such as concrete additives or fuel for paper mills. Significant research efforts are devoted towards the disruption of lignin into its monomers with the aim to create high-value applications. This task remains challenging due to the heterogeneity of lignin and the harsh conditions needed to degrade the covalent bonds linking the monomers together. Our approach instead takes advantage of this intrinsic stability of lignin by further polymerizing lignin building blocks on surfaces to form organic coatings. These coatings consequently alter the surface properties of these substrates in a simple, scalable, versatile and renewable fashion.

BI-TuP2 Flash Networking Poster: Characterising Hydrogel Chemistry Through Low Temperature ToF-SIMS

Michael Taylor, *D. Scurr*, The University of Nottingham, UK, *M. Lutolf*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Swtizerland, *L. Buttery*, *M. Zelzer*, *M.R. Alexander*, The University of Nottingham, UK

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

BI-TuP3 Flash Networking Poster: Molecular-Level Insights into the Wet Adhesion Mechanisms of the Lady Beetle (*Cocinella septempunctata*)

James Fowler, Oregon State University, *J. Franz*, Max Planck Institute for Polymer Research, Germany, *S. Gorb*, University of Kiel, Germany, *T. Weidner*, Max Planck Institute for Polymer Research, Germany, *J.E. Baio*, Oregon State University

Humans have always marveled at the ability of insects to cling and climb along virtually any surface – whether it’s vertically up a wall or upside-down supporting masses orders of magnitude greater than their own. Many insects have adapted to a range of environmental surfaces by evolving a wet adhesion process that combines an expansive array of hairy contacts on their feet, known as setae, and an adhesive fluid that forms contact between the setae and a substrate. Previous studies of this adhesion mechanism have focused almost exclusively on the mechanical and kinematic aspects of adhesion, and not on the molecular interactions at the fluid – substrate interface. In the work presented here, we probe the molecular interactions between the adhesive fluid taken from lady beetles (*Cocinella septempunctata*) on two model substrates (deuterated-PMMA and deuterated-polystyrene) with vibrational sum frequency generation (SFG) spectroscopy and scanning electron microscopy (SEM). High-resolution SEM images of individual seta-fluid footprints on both sets of surfaces indicate localized water-oil emulsion de-wetting with no sign of distinct patterning within the footprint. SFG spectra collected at the C-H stretching region (2800-3100 cm^{-1}) contain peaks at 2848 cm^{-1} and 2867cm^{-1}, characteristic of symmetric CH_2 and CH_3 stretches, respectively. For the fluid on both the PMMA and polystyrene, we observe a large ratio of the 2867/2848 cm^{-1} peaks suggesting a well-ordered hydrocarbon monolayer with methyl groups oriented normal to the substrate. Spectra at the amide I stretching region (1500-1800 cm^{-1}) collected from the PMMA-fluid sample contain a single peak at 1700 cm^{-1} indicating the presence of ordered free fatty acids; however, this signal is absent from the polystyrene-fluid spectra. Combined, this set of SFG spectra demonstrate that during adhesion to a polar surface, fatty acids within the fluid form a highly ordered layer at the substrate surface. While on a non-polar surface, the mechanism changes and some other hydrocarbon species present within the fluid orders at the interface.

BI-TuP5 Flash Networking Poster: Structured Noble Metal Nanosurfaces for Biosensing and Bioanalysis (1): Controlling Galvanic Displacement Reaction for Creation of Silver Nanostructures

Shingo Yoneda, Toyo University, Japan, *T. Okamoto*, RIKEN, Japan, *H. Vieker*, *A. Beyer*, *A. Gölzhäuser*, Bielefeld University, Germany, *H. Takei*, Toyo University, Japan

There has been an increasing interest in creating silver nanostructures for optical analytical techniques such as surface-enhanced Raman spectroscopy. Galvanic displacement reaction, exploiting the difference in ionization tendency of different metals, can be used for such purposes, but previously there was not much room for controlling the final morphology of nanostructures when bulk metal was simply treated with silver nitrate solution. However, recently it was reported that use of copper colloids rather than bulk copper allows finer structural controls. We have also found that surface-adsorbed copper structures can be transformed to silver nanostructures with various morphologies. The size and amount of copper were crucial for the morphology of the final structures. Recently we have also begun experimenting with addition of polyvinylpyrrolidone (PVP) to the silver nitrate solution because PVP was known to affect the morphology of the silver nanostructures with the conventional galvanic displacement reaction using bulk metal. Here we describe its results.

Our base metal nanoparticles are formed by evaporation of a base metal on surface-adsorbed monodisperse SiO_2 nanospheres. Variable parameters are the metal deposition thickness and the nanosphere diameter. We treated these base metal nanoparticles with an aqueous silver nitrate solution containing PVP. In this experiment, we investigated effects of changing the concentration of PVP, the molecular weight of PVP (K15, K30, K90), and the deposition thickness of copper (10, 30, 60 nm). For evaluation of the structures, we observed their morphologies with SEM and obtained Raman spectra of 1 mM rhodamine 6G, R6G.

Use of PVP leads to silver nanostructures with different morphologies. When PVP is used, massive silver nanostructures are formed. When not, however, silver nano-filaments are formed instead. It was also confirmed that the form of silver nanostructres is dependent on the molecular weight of PVP used and the deposition thickness of the original base metal. When these nanostructures are used as a substrate for SERS, the enhancing effect becomes greater when prepared with PVP.

BI-TuP7 Preparation of Bioglass-ZrO_2 Functionalized Coatings by EPD

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Surface functionalization is an important tool for many technical and biomedical applications. The modification of a nanoparticle surface can alter its adhesion characteristics, improve the dispersion in matrices or enhance catalytic properties. In this work, strategies for surface functionalization of inorganic materials with a special focus on zirconia (ZrO_2) synthetized nanoparticles as reinforcement for bioglass ceramic matrix are discussed. The density of functionalization in nanoparticles using different organosilanes molecules was measured by Si–O and hydroxyl (–OH) bonds. The reactivity between organosilanes and the surface of nanoparticles was measured by electrostatic potential using molecular simulations with Gaussian software. This simulation showed the regions from silane molecules with the lowest electrostatic potential representing the sites were the metallic oxides are attached. The morphology of nanoparticles and functionalization layer was characterized using TEM-EDS, FTIR and TGA. Due to the low stability of bioglass in organic suspensions, the modification of its surface was necessary using functionalized nanoparticles which allowed the preparation of Bioglass-ZrO_2 reinforced composites. Suspensions were prepared using ethanol as dispersing media. Bioglass suspensions showed poor stability, while suspensions with Bioglass and functionalized nanoparticles showed improved stability. The formation of bonds between bioglass particles and functionalized ZrO_2 nanoparticles allowed the dispersion of the material which is necessary for the preparation of coatings by Electrophoretic Deposition (EPD). The Bioglass and Bioglass-ZrO_2 coatings were characterized by SEM-EDS and XRD. A uniform coating was obtained with well dispersed ZrO_2 nanoparticles. These coatings using functionalized ZrO_2 as reinforcement can improve the mechanical properties as well as the biocompatibility of the composite.

BI-TuP9 Flash Networking Poster: Gold Nanoparticle-Delivered RNA Genetic Control Devices, ***Michael Newton***, *J.M. Carothers, D.G. Castner*, University of Washington

Gold nanoparticles (AuNPs) promise to offer a minimally toxic, easily modifiable, and high payload carrying drug or biologic delivery agent. Despite this promise and the emphasis placed on their intrinsically high surface area to volume ratio, surface functionalized AuNP conjugates in biomedical applications often lack detailed surface characterization. Consequently, there is little experimental validation of a surface attached ligand's orientation or conformation. Nucleic acids are one such ligand and biologic diagnostic or therapeutic agent currently being investigated. RNA-based logic circuits responsive to small molecules, endogenous proteins, and miRNAs have been demonstrated to diagnose the state of a cell and implement a programmed therapeutic outcome. A truncated RNA circuit such as this could benefit from local targeting and concentrated delivery on a nanoparticle platform and prove more effective. Proper tools and techniques to characterize biomedical AuNP conjugates would inform their design and result in better understanding the observed cellular uptake, efficacy, toxicity, and clearance.

Short single-stranded DNA oligo's on AuNPs have been used to sense a complementary nucleic acid, or as a capture strand to facilitate assembly of larger constructs. Additionally it is often recognized that the method of attachment and incorporation of spacers will play a factor in the assembled conjugate's performance. A thiol attachment to Au is often used with a polynucleotide spacer for simple assembly and increased performance. These investigations typically neglect to consider other types of spacers like ethylene glycol chains of various lengths. We will compare the polynucleotide and ethylene glycol spacers used individually and jointly in a single-stranded DNA capture oligo conjugated AuNP in terms of particle surface characterization and nucleic acid functionality. This will be realized through X-ray Photoelectron Spectroscopy and Localized Surface Plasmon Resonance in conjunction with standard bulk characterizations like Dynamic Light Scattering, Electrophoresis, and Transmission Electron Microscopy, and through incorporation of strand-displacement and RNA aptamer nucleic acid devices with distinct programmed fluorescent outputs from a specific small molecule or oligo input.

BI-TuP11 Flash Networking Poster: Exhaled Breath Analysis of Ammonia Gas using Colorimetric Attenuated Total Reflectance Spectroscopy, ***MariaAntoaneta Bratescu***, *K. Isawa,* Nagoya University, Japan*, T. Kiguchi,* Shibaura Institute of Technology, Japan*, O.L. Li, N. Saito*, Nagoya University, Japan

The identification of exhaled breath volatile organic compounds represents a metabolic biosignature with the potential to recognize some diseases. There are various techniques to analyze exhaled breath gases, as spectrometry, gas chromatography, and spectroscopy. The recent trend towards breath analysis instruments has led to the development of fully integrated prototypes of point-of-care devices.

In this research we develop a miniature sensor using attenuated total reflectance spectroscopy to detect breath gases in the range of hundreds ppb. A 0.2 mm thick, 20 mm wide, 65 mm long, fused silica plate with 60° beveled edges (Shin-Etsu Quartz Products, Inc.) was used as the internal reflection element (IRE).[1] The IRE surface was coated with the chemical sensor specific to one of the gases from the breath, embedded in a polymer, using a layer-by-layer electrostatic assembly method. The evanescent light produced by multiple total internal reflections penetrates a few tens of nanometers in the film leading to a high detection sensitivity.

For ammonia gas detection Poly(diallyldimethylammonium chloride) (PDDA, Mw: 200000-350000, 20 wt% in H_2O) and tetrakis(4-sulfophenyl)porphyrin (TSPP, Mw: 934.99) were used as polymer and chemical sensor, respectively.[2,3] The detection consists in measuring the decrease of light intensity of the Soret band of the porphyrin molecule around 483 nm under the chemical reaction with ammonia. First we recorded absorption spectra through the IRE using a broadband visible light source and a spectrograph for different film conditions and ammonia concentrations. Then the broadband light source and the spectrograph were replaced with a 450 nm light emitting diode (LED) and a photodiode (PD). The ammonia sensing capability of the porphyrin film was tested in both liquid and gas phases and a 500 ppb detection limit was found. We studied the ammonia gas detection limit in dependence with the number of layers of the chemical sensor and the polymer deposited on the IRE surface. AFM measurements show the surface modifications after the ammonia gas adsorption on the chemical sensor film. Stability, reversibility, and the humidity influence will be discussed.

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[2] K. S. Suslick, et al., An optoelectronic nose for the detection of toxic gases, Nature Chemistry, 1, 562, 2009.

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BI-TuP12 Flash Networking Poster: Structured Noble Metal Nanosurfaces for Biosensing and Bioanalysis (3): Surface-Enhanced Fluorescence Detection with Cap-shaped Silver Nanoparticles, ***Miki Ebisawa***, *T. Kawakami, H. Takei*, Toyo University, Japan

OBJECTIVE

Surface-enhanced fluorescence, SEF, is a highly sensitive method for detecting fluorescent molecules using a noble metal structure. We used cap-shaped silver nanoparticles that were fabricated by vacuum deposition of silver onto a dense layer of silica nanoparticles immobilized on a glass slide. While there is much in common with surface-enhanced Raman spectroscopy, SEF requires that molecules be placed at a certain distance away from the metal surface in order to avoid quenching. To satisfy this requirement, we have evaluated the effect of introducing a dielectric layer on the substrate surface. Furthermore we have investigated a number of techniques for patterning different antibodies or DNA fragments as we are targeting immunoassay and DNA diagnosis for the application of SEF, up to several dozens of different target molecules at the same time.

METHODS

Cap-shaped silver nanoparticles prepared with the above method were soaked in a silane coupling agent (tetraethylorthosilicate, TEOS) to form a dielectric layer. With DNA measurements, we used a probe DNA (19 mer) and FITC-labeled target DNA (13 mer). After immobilization of the probe DNA, the target DNA was made to hybridize. We examined two methods for patterning. One way was to prepare polymer fibers at whose end silver nanoparticles were formed. Fibers modified with different capture molecules were bundled together to be used for measurements. As a second method, after a substrate surface was uniformly modified by a single type of capture molecule, the molecule was locally destroyed: a "subtractive" method. For destruction, ozone treatment or additional deposition of silver was used.

RESULTS

From results by a microarray scanner, we confirmed that the signal intensity of the fluorescent modified DNA from a silver nanoparticle substrate with a dielectric layer was more than doubled compared with the control substrate, demonstrating the effect of a dielectric layer. As for the ozone cleaning, the treatment of the substrate enhanced the signal intensity if applied prior to adsorption of the target molecules; if afterward, the same treatment was found to diminish the signal, as we expected. However, the effect of additional silver deposition was unexpected. We assumed that the signal would be diminished by additional deposition several nm in thickness, but on the contrary the signal was enhanced by additional deposition, the signal intensity being maximized when the thickness was 150 nm. In the future, we will examine this phenomenon in greater detail, with a hope of obtaining a fundamental insight into the mechanism of SEF.

BI-TuP13 Flash Networking Poster: Structured Noble Metal Nanosurfaces for Biosensing and Bioanalysis (2): Localized Surface Plasmon Resonance Sensor Operating in the Near-IR Regime, ***Takumi Miyashita***, *N. Bessho,* Toyo University, Japan*, T. Okamoto,* Riken, Japan*, H. Vieker, A. Beyer, A. Gölzhäuser,* Bielefeld University, Germany*, H. Takei*, Toyo University, Japan

Noble metal nanoparticles possess an optical extinction peak due to localized surface plasmon resonance, LSPR. The peak shifts when the refractive index in the immediate vicinity changes, a useful property for making biosensors. While there are numerous ways to prepare noble metal nanostructures, we find that evaporating a noble metal on a surface coated with a monolayer of monodisperse silica nanospheres is a convenient method. With the above method, it is easy to form highly dense nanostructures, with the extinction peak in excess of O.D. 2. The spectrum can be readily modified by varying the sphere diameter and metal deposition thickness. While this method has been used by a number of groups, we found that resulting structures possess not only a peak in the visible but also an additional peak in the near-IR. The latter peak has four times the sensitivity of the peak in the visible.

There are many ways to use LSPR sensors other than the traditional antigen-antibody monitoring. One has to do with improving a colorimetric diagnostic method. Often it is implemented in the form of immunochromatographic assays, ICA. It is, however, used mostly only for qualitative assays, such as detection of flu. We believe that bestowing it with a quantitative detection capability as well as an increased dynamic range would further boast the use of ICAs. In some colorimetric assays, an enzyme is used to generate a colored product. By using the alkaline phosphatase-NBT/BCIP system, here we describe various techniques for maximizing the interaction between the enzymatic reaction product and the sensor surface. Another application is detection of nanoscopic gas bubbles. If bubbles form on the sensor surface, even with the size of 5 nm or less, it should lead to a detectable shift of the peak. We have decided to test this concept on detection of useful microorganisms from soil samples obtained below the ocean bed where very few are expected. Our strategy is to look for catalase which is secreted by practically every life form. When catalase, captured on the sensor, reacts with H_2O_2, oxygen bubbles form so that the presence of microorganisms can be potentially detected by monitoring bubble formation. Another set of experiment involves monitoring of vascular endothelial cells in the presence of elevated amounts of glucose. We have cultivated VE cells on our LSPR sensor. It is our intention to use the sensor signal for monitoring changes in the morphology of cells induced by glucose, leading to a better understanding of diabetes.

BI-TuP14 Flash Networking Poster: Exploration of Conformational Changes of Nucleic Acids as a Function of Interactions with Histone-mimic Nanoparticles using All-atom Simulations, ***Yaroslava Yingling****,* *J.A. Nash*, North Carolina State University

Nucleic acid based nanotechnology and gene therapy approaches depend on the compaction, or packaging, of the nucleic acids DNA and RNA. Though there has been much experimental work on the interactions of DNA with proteins, the atomic details of DNA-nanoparticle binding remain to be comprehensively elucidated. Even less is known about the binding of double stranded RNA with cationic molecules. Here, we report the results of a comprehensive large scale all-atom molecular dynamics simulation investigation of the binding ligand-functionalized gold nanoparticles (NPs) binding to the nucleic acids double stranded DNA and RNA as a function of NP charge and solution salt concentration. Our simulations show that low charge NPs bind to DNA and cause little distortion of the DNA helix, however, nanoparticles with charges of +30 or higher cause DNA to bend and wrap in a way similar to nucleosome. Moreover, shape of the NP ligand corona plays an essential role in quality of DNA wrapping. The nanoparticles cause different behavior with short segments of RNA in that they are not able to induce bending for even the most highly charged nanoparticles in 0.1M NaCl. To compact RNA, a combination of highly charged nanoparticles with low salt concentration is required. Results from this paper can be used for future design of efficient NP vectors for gene delivery and other biomimetic materials.

BI-TuP17 Flash Networking Poster: Nanoscale Structures in Live Cells Visualized through High Resolution Imaging and Mechanical Property Mapping, ***Bede Pittenger***, Bruker, *H. Schillers,* Univ. Muenster*, A. Slade, J. Shaw, S. Hu, I. Medalsy, T. Mueller*, Bruker

Nanoscale structures on or just beneath the cell surface often strongly influence cell function. Atomic Force Microscopy allows measurement of both topography and mechanical properties of these structures on live cells at resolutions far below the diffraction limit. When integrated and synchronized with optical microscopy (including fluorescence, confocal microscopy, and super-resolution imaging) AFM provides new methods of studying the relationship between cell structure and function in near-physiological conditions.

One class of these nanoscale structures is the microvillus -- a structure commonly found on epithelial cells. Epithelial cell function is coupled to the density of microvilli and degradation can cause malabsorption and diarrhea [1]. Observing the both tiny and very flexible structures such as microvilli on the apical surface of a live cell has been very challenging because the native microvilli structures are displaced and deformed by the interaction with the AFM probe.

Another class of nanoscale structure within cells is the actin fibril. These structures make up the actin cytoskeleton and are thought to play an important role in many types of cancer [2]. AFM allows observation of the actin fibrils, their position and their stiffness. PeakForce Tapping (with PeakForce QNM) provides fast, high resolution, quantifiable maps of the distribution of the actin fibrils in the cytoskeleton.

In this talk we will present the first images of microvilli on the membrane surface of living kidney cells obtained by AFM. Because the data was collected with PeakForce Tapping, it is possible to compare the response of the microvilli to different applied forces, and observe the effect of force on microvilli structure. Finally, we will also present mechanical maps of live MDCK cells showing the distribution and stiffness of individual actin fibrils.

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Electronic Materials and Processing
Room: Hall 3 - Session EM-TuP

Electronic Materials and Processing Poster Session

EM-TuP1 Ionic Liquid Gated Electric Double Layer Transistors based on a-IGZO Thin Films*,* ***PushpaRaj Pudasaini****, J.H. Noh, A. Wong, A.V. Haglund,* The University of Tennessee Knoxville*, S. Dai, T.Z. Ward,* Oak Ridge National Laboratory*, D. Mandrus,* University of Tennessee, Knoxville and Oak Ridge National Laboratory*, P.D. Rack*, The University of Tennessee Knoxville

The electric filed effect with the field effect transistor configuration is a powerful approach for externally tuning the carrier density of a material and investigating associated changes in the electronic properties of the material. To this end, ionic liquid gated field effect transistors have been extensively studied due to their low operation voltage, ease of processing and the realization of high electric fields at low bias voltages. Herein, we report ionic liquid (IL) gated field effect transistor based on amorphous Indium Gallium Zinc Oxide (IGZO) thin film active layers. The transport measurement of the IL revealed the intrinsic n-channel property of the IGZO thin film with high ON/OFF ratio $\sim 10^5$ and a large field effect electron mobility of 5.38 $cm^2V^{-1}S^{-1}$ at 300K and a threshold voltage of 0.1V. Comparable measurements on the bottom SiO_2 gate insulator revealed an ON/OFF ratio $\sim 10^9$ and field effect electron mobility of 12.53 $cm^2V^{-1}S^{-1}$ and a threshold voltage of 2.5V. Furthermore, we found that the ionic liquid gating of a-IGZO thin film leads to not only an electrostatically induced carrier accumulation but also the field induced creation of O_2 vacancy, with constituent migration of oxygen in and out of the film depending on the polarity of the bias used. This could leads to the bias induced control of carrier density in an amorphous oxide semiconductors.

EM-TuP2 Resistor Thermal Noise Rectification for Energy Harvesting, ***Amina Belkadi****, S. Joshi,* University of Colorado at Boulder*, G. Moddel*, University of Colorado at Boulder and Redwave Energy

Resistor noise produces real power and can, in principle, be rectified for thermal energy harvesting. For ambient temperatures and above, the peak frequency in the noise spectrum is at least 30 THz, which requires an ultra-high-speed diode for rectification and a quantum-based theory to describe the rectification process. In this study, we analyze harvesting energy through the rectification of resistor thermal noise. The electrical noise spectrum generated by a warm resistor is similar to that from one-dimensional blackbody radiation channeled through an antenna. This allows the use of optical rectenna circuitry and concepts, in the presence of a temperature gradient between the resistor and the diode, by merely replacing the antenna with a resistor. We use the semi-classical theory of photon-assisted tunneling to explain the diode rectification behavior. In contrast to an antenna-coupled diode, using a resistor modifies and may help resolve some optical rectenna challenges such as the RC time constant and optical coherence limitations, impedance matching to the diode, and undesired heating of the diode. However, a key challenge remains: the very low power produced by the hot resistor. This limits the diode rectification efficiency. If challenges of low power and low rectification efficiency are overcome, the concept can be used for applications such as (i) efficient harvesting of energy from waste heat sources and even from the earth, when a suitable heat sink is provided, and (ii) conversion of solar energy either directly or via an intermediate thermal transducer. The fact that conventional photovoltaic devices use only the high energy part of the solar spectrum to produce power places a limit on their conversion efficiency. Therefore, integration of solar cells with a resistor-based thermal noise energy harvesting device could potentially increase the overall efficiency of solar cells.

EM-TuP5 Electrical and Optical Properties of the Porous Nickel Oxide Thin Film as Counter Electrode for the Application to Electrochromic Devices, ***WonChang Lee**, J.U. Wie, E.C. Choi, B.Y. Hong*, Sungkyunkwan University, Republic of Korea

Electrochromic materials are able to change the optical properties persistently and reversibly by an external voltage. Applications of electrochromic materials include rearview mirrors, smart windows, display panels, etc. A large number of transition metal oxides such as the well-known tungsten trioxide (WO_3) cathodic material, which reversibly switches from transparent to blue upon lithium or proton insertion.

In contrast, nickel oxide (NiO) is an anodically coloring material but despite promising features such as high coloration efficiency, good optical memory and cost effectiveness. NiO is often used as a secondary electrochromic material to complement cathodically coloring WO_3 in prototype electrochromic devises. Because NiO have for a long time attracted attention as counter electrode regarding their brownish color in the oxidized state that, together with the blue color of the reduced WO_3, yields a neutral gray color device in the colored state. The electrochromism in NiO films is rather complicated although it is generally accepted that the reversible transition between colored and bleached states is related to redox process between the NiOOH and NiO. Moreover, owing to their rapid degradation on cycling, difficulties in using nickel oxide films have been encountered. However, the problems of NiO thin films that limit their commercialization and poor durability are still debated. When NiO film is formed as porous structure, the surface area to the volume ratio is large and the same probably lead to an increase in the ion intercalation and deintercalation. The large-area surface of the porous film structure can be helpful for the augmenting the optical modulation.

In our study, the porous NiO thin film was deposited using sol gel-method and dip-coating technique on the Indium Tin Oxide (ITO) glass. The NiO thin film was formed by annealing process at different temperatures after the dip-coating technique. Studies on the effect of annealing temperature to improve the crystallinity and the electrochromic properties of the NiO thin films have been carried out. So, we confirmed that the electrochromic efficiency was improved by optimizing of the annealing condition.

EM-TuP6 Tunable Optical Extinction of E-Beam Fabricated Nano-Rectennas Modified by Atomic-Layer Deposition, ***Raymond Wambold**,* The Pennsylvania State University, *G.J. Weisel, D.T. Zimmerman,* The Pennsylvania State University, Altoona, *J. Qi, B.G. Willis*, University of Connecticut

We present a systematic study of plasmon extinction characteristics of arrays of tunable nanoscale rectennas, which have possible application as solar-energy harvesting devices and optical-IR sensors. Each nanorectenna is composed of a triangular prism and a flat counter-electrode, both made of palladium. We fabricate arrays of rectennas on silica using standard electron-beam lithography. We then use atomic-layer deposition (ALD) of copper to control the gap distance between the two electrodes. To measure optical extinction we employ a broadband (Quartz-tungsten-halogen) light source in a confocal, transmission arrangement. Our measurements demonstrate that the plasmon extinction resonance can be tailored by varying the e-beam dose and the cycles of ALD. The most important feature of our work is the ability to reduce the gap spacing between the two electrodes, which serves to systematically redshift the extinction peak and ultimately bring the two electrodes into the tunneling regime. We also investigate the effects of overall size, morphology, and material properties on the extinction resonance. We employ Finite-Difference Time-Domain simulations to support our device design and to corroborate our experimental measurements. In addition, we use scanning electron microscopy to correlate the device-dimension and morphology changes to the plasmon extinction characteristics.

EM-TuP7 The Study of Light Control using Nanoantenna, ***JeongHee Shin**, S. Kim, J.E. Jang*, Daegu Gyeongbuk Institute of Science and Technology (DGIST), Republic of Korea

Recently, the antenna has been scaled down to nanometer to absorb higher electric-magnetic wave. Traditionally in communication area, high frequency is required to transmit or receive much more information. Nanometer antenna is different from general antenna in communication area due to properties and applications. Nanoantenna can cover the visible to near-infrared (NIR) wavelength regions; thus, it has a lots of applications in communication, optics, bioelectronics and so forth. Especially in optics area, not only the light control but also structure-depended absorption, reflection, and transmission using nanoantenna have been studied. The light absorption using nanoantenna can be useful to harvest electrical energy instead of solar cells expected to be much higher efficiency as well. The optical properties of nanoantenna can be affected by geometry factors such as structure, shape, and pitch. It cannot correspond traditional antenna theory due to surface plasmons (SPs) which are coherent delocalized electron. This penomenons exist at the interface between two materials, strong couplings between electrons on metal and incident light. Designing nanoantenna is much more complicate than that of general antenna so that it does not simply follow conventional antenna theory. To apply the nanoantenna to various applications, the study of parameters to define optical properties in nanoantenna should be necessary. We focused on control of color via nanoantenna depending on various geometries. First of all, we investigated the relation between parameters and color change. We can design the target peak wavelength in visible region. Then, we will report optical transistor to control colors. It can be applied to various applications such as color filter, next-generation display, energy harvesting system with higher efficiency, and so on.

EM-TuP8 MIM: Role of Design and Fabrication, ***Aparajita Singh**, S. Bhansali*, Florida International University

The early assumptions have been that thin-film development and contact area the two major issues in defining characteristics of the MIM tunnel diode. Based on this the focus has rigorously been on patterning and various thin-film deposition techniques for MIM formation. Several designs with varied fabrication methods have been considered for fabrication of MIM devices till date for applications like energy-harvesting devices, terahertz electronics, macro electronics, etc. Here we elaborate upon each design and associated fabrication challenges for Ni-NiO based MIM and MIIM diodes. The goal is to optimize the MIM device design for: (1) ease of integration with other circuit devices, and (2) simpler fabrication steps for minimizing alteration in oxide property and inherent device impedance. Fabrication issues such as material selection, metal deposition, oxide growth/deposition, and patterning are discussed. Since ALD is currently the leading way to provide uniform, pinhole free and ultra-thin oxide layers, we present a comparison of oxide properties deposited by sputtering and ALD (the leading techniques) along with their impact on I-V characteristics. Influence of surface preparation on oxide and growth/deposition temperature are also discussed.

EM-TuP9 Comparison of Hafnium Oxide and Zirconium Oxide Thin Films for Fabricating Electronic Devices, ***Jouantrey Spence**, F. Cunningham, R. Moten, Z. Xiao*, Alabama A&M University

Thin films of hafnium dioxide (HfO_2) and zirconium oxide (ZrO_2) are used widely as the gate oxide in fabricating integrated circuits (ICs) because of their high dielectric constants. In this research, we report the growth of hafnium dioxide (HfO_2) and zirconium oxide (ZrO_2) thin films using e-beam evaporation, and the fabrication of complementary metal-oxide semiconductor (CMOS) integrated circuits using the HfO_2 and ZrO_2 thin films as the gate oxide. MOSFETs, CMOS inverters, and CMOS ring oscillator were fabricated, and the electrical properties of the fabricated devices were measured. The measurement results on the devices fabricated with the two films were compared, and will be reported in the Conference.

EM-TuP10 Non-Equilibrium First-Principles Study on Electron Scattering Processes in Magnetic Tunnel Junction, ***Masaaki Araidai**,* Nagoya University, Japan, *T. Yamamoto,* Tokyo University of Science, Japan, *K. Shiraishi*, Nagoya University, Japan

Investigation of magnetic tunnel junction (MTJ) is a key issue for the development of advanced magnetoresistive random access memories (MRAMs). MTJs consist of two metal ferromagnets, thick magnetization-fixed and thin magnetization-free layers, separated by a thin insulator, and they exhibit two resistances, low or high, depending on the relative direction of the magnetizations of fixed and free layers, parallel (P) or antiparallel (AP) configuration. The simplest way to reverse the magnetization of free layer is switching by external magnetic fields. However, absolute currents required for the magnetic-field switching do not scale with reducing the junction size. At present, current-induced magnetization switching (CIMS) proposed by Slonczewski [1] and Berger [2] is drawing attention as the most promising candidate for a mechanism of magnetization reversal of free layer, owing to the scalability of CIMS [3]. Although CIMS has been successfully applied to the operation of MRAM, it has not been sufficiently understood yet.

In this work, we investigated electron scattering processes in CIMS of a MTJ by the non-equilibrium Green's function technique coupled with the density-functional theory [4]. We employed a Fe/MgO/Fe MTJ sandwiched between ferromagnetic Fe and paramagnetic Ta electrodes, as a typical MTJ model. The current-voltage characteristics indicated high tunnel magnetoresistance of the MTJ (about 600% at zero bias) and was highly antisymmetric with respect to the bias voltage, originating from the antisymmetric structure and the magnetization configuration. We found from the current density dependence of magnetization of the free layer that the switching from AP to P configuration could be realized by lower electrical power than P-to-AP case. From detailed analyses of the density of states subject to a finite bias voltage, we clarified that the asymmetric behavior originates from the difference in the electron scattering processes between switching directions.

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EM-TuP11 First Principles Study on Switching Mechanism of Superlattice (GeTe)$_2$/Sb$_2$Te$_3$ Phase Change Memory*, **Masayuki Takato,** H. Shirakawa, M. Araidai, K. Shiraishi*, Graduate School of Engineering, Nagoya University, Japan

Superlattice phase change memory (superlattice PCM) consisting of (GeTe)$_2$/Sb$_2$Te$_3$ stacked structure is one of the most promising candidates for next-generation non-volatile memories and has received considerable attention in recent years [1,2]. The memory operations are attributed to small structural change between two atomic configurations before and after switching. Therefore, the energy required for switching between higher and lower resistive states is much lower than that of conventional PCMs utilizing phase transition between crystal and amorphous phases [3]. However, the reaction pathway in switching of superlattice PCM has not yet been clarified and the detailed analyses of the structural transition between high-resistive and low-resistive states are prerequisites for fully understanding the switching mechanism.

In this work, we investigated the switching process of the superlattice (GeTe)$_2$/Sb$_2$Te$_3$ PCM using the first-principles electronic states calculations. The atomic structures and the electronic states were calculated by VASP code [4], which is based on density functional theory with the plane-wave basis sets, a PBE-type exchange-correlation functional and the projector augmented-wave method. For the calculations, $\boldsymbol{k}$ points of 8 x 8 x 4 Monkhorst-Pack grid were used and the cutoff energy was 500eV.

We found that atomic configurations of high-resistive and low-resistive states are not stable but metastable [5]. Therefore, the superlattice (GeTe)$_2$/Sb$_2$Te$_3$ PCM can do cyclic operations due to the metastability. In addition, we clarified the structural transition process between high-resistive and low-resistive states. I will show the detail process in the announcement. Furthermore, the validity of our proposal will be shown from the detailed analyses of the potential energy surface and electron-density distribution.

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EM-TuP12 First Principles Study on Atomic-scale Behavior of N, H Atoms and O Vacancy Related Defects in SiO$_2$ Layer of MONOS Memories*, **Hiroki Shirakawa,*** Graduate School of Engineering Nagoya University, Japan*, M. Araidai,* Graduate School of Engineering, Nagoya University, Japan*, K. Kamiya,* Center for Basic Education and Integrated Learning, Kanagawa Institute of Technology, Japan*, K. Shiraishi*, Graduate School of Engineering, Nagoya University, Japan

Metal-Oxide-Nitride-Oxide-Semiconductor (MONOS) memories have attracted a great attention as one of the next generation NAND flash memories. MONOS memories can trap charges inside defect sites in charge trap layers (SiN) that are spatially separated each other, leading to great merits for integration techniques such as 3D-structure and multi-level-cell operation. On the charge trapping layer in MONOS memories, it has been reported that large amounts of O and N atoms are incorporated into SiO$_2$/SiN interfaces, leading to the formation of electron occupied defects near the interfaces [1]. In addition, Vianello et al. have found that a lot of H atoms distribute in SiO$_2$, SiN and interface [2]. Yamaguchi et al. have also reported atomic-scale behavior of such defects in MONOS SiN layers during program/erase (P/E) cycles [3]. However, for SiO$_2$ layer of MONOS memories, the decisive atomic-scale information has not been clarified yet.

In this work, we investigate the behavior of N, H atom and O vacancy in SiO$_2$ during P/E cycles using VASP code [4], which is based on the density functional theory with GGA of Perdew-Wang-91. Core valence interactions were described by the ultrasoft pseudo potential. To simulate N related defects in SiO$_2$ layer near SiN/SiO$_2$ interface, we employed the 72 atoms super-cell of α-quartz including the defects. The defects formed by substituting two N atoms for two O atoms in SiO$_2$. The P/E operations correspond to the electron and hole injections into the defects in our calculation.

We found that O vacancies are induced by the two N-substituted defects, forming the complex defect (VoN2) that consists of one O vacancy and two N atoms. Then, VoN2 defect cannot traps charges when the Fermi energy of MONOS is within the ranges of SiN band gap. We also found that the diffusing H atoms in SiO$_2$ change the characteristics of VoN2 defect. VoN2 defect is transformed to another defect including H atoms (VoN2-H) by adsorbing hydrogen atoms. While VoN2-H defect is energetically unstable compared with VoN2 in the neutral charge state, VoN2-H defect becomes very stable in the negative charge state. This indicates that VoN2-H defect is able to trap electrons.

These results suggest that the amount of trapped charges on MONOS memories strongly depends on the dynamics of H atoms in SiO$_2$ during P/E cycles; namely, the thermal diffusion of H atoms would bring about the threshold voltage shift of MONOS memories.

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EM-TuP14 Hybridization and Characterization of Reduced Graphene Oxide with Copper Nanoparticles*, J.D. Lee, L.R. Hubbard, **Anthony Muscat***, University of Arizona

An in-situ crystallization technique was used to prepare a hybrid containing Cu nanoparticles (NPs) bound to reduced graphene oxide (rGO) sheets. The hybrid material was investigated with scanning electron microscopy (SEM), Raman spectroscopy, ultraviolet visible spectroscopy (UV/vis), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FTIR). SEM results show that spherical Cu nanoparticles ranging from 1.6 to 7.4 nm in diameter and agglomerates were randomly dispersed on rGO sheets. SEM images show that Cu NPs were intercalated between rGO sheets to form a hybrid material. UV/vis of the rGO:Cu hybrid contained peaks associated with GO and Cu NPs with a blue shift in the peak resulting from n→pi* transitions of C=O bonds to 283 nm and a red shift in the peak indicative of the Cu surface plasmon resonance to 585 to 630 nm. XPS confirmed the presence of CuO and Cu(OH)$_2$ with peaks at 933.4 and 934.5 eV respectively. The presence of imidazole, from the ionic liquid [Bmim][BF$_4$] used to synthesize the Cu NPs, was confirmed by the XPS peak found at 400.4 eV and the contributions to fingerprint regions in the FTIR. The as synthesized rGO:Cu hybrid had an electrical conductivity of 3.5*10^6 S/m. This value is intermediate between GO with a baseline of 0.04 S/m and Cu NP thin film conductivity of 2.0*10^7 S/m.

EM-TuP15 Hybrid Transparent Conductive Electrodes Embedded with Pt Nanoclusters for Reliable and Efficient GaN-based Light-Emitting Diodes, *K. Kim, **Hyunsoo Kim***, Chonbuk National University, Republic of Korea

A key technology to fabricate highly efficient and reliable GaN-based light-emitting diodes (LEDs) is transparent conductive electrodes (TCEs), which are used as the Ohmic contact to *p*-GaN and the current spreader. Indeed, a lot of attempts have been made to fabricate better TCEs with high optical transmittance, low sheet resistance, and low contact resistance by employing Pt, oxidized Ni/Au, indium tin oxide (ITO), zinc oxide (ZnO), carbon nanotubes, graphene, et c. Among these TCEs, ITOs are the best in terms of their high optical transmittance in the visible wavelength range, low sheet resistances, feasible Ohmic contact to *p*-GaN, and guaranteed robustness, enabling them to be practically used in commercial products. Unfortunately, however, the sputtering process, which can produce the best quality of ITO films, cannot be used for the deposition of ITO film to p-GaN, associated with the sputtering damage of *p*-GaN surface. As an alternative, therefore, the *e*-beam evaporation technique, which is a representative physical vapor deposition technique free of ion damage, has been used for the ITO deposition. However, the evaporated ITO films were relatively poorer than the sputtered films due to the lack of stoichiometry and insufficient crystallinity of the ITO.

Metallic Pt thin film was shown to act as efficient current spreader in the GaN-based LEDs due to its low R_{sh} value and feasible Ohmic contact associated with its large work function (5.65 eV). More interestingly, Pt thin film has a distinctive feature of agglomeration upon thermal annealing, a so-called Ostwald ripening, leading to the formation of Pt islands or nanoclusters. This feasibility suggests that the combination of sputtered ITO or ZnO films and Pt nanoclusters, namely, hybrid TCEs, may be successful for fabricating novel TCEs for GaN-based LEDs since Pt nanoclusters are expected to act as the preventer of ion damage or an Ohmic patch. In this regard, hybrid TCEs were investigated by combining Pt nanoclusters and sputtered films. Notably, hybrid ITO TCEs fabricated by combining interfacial Pt nanoclusters with a coverage ratio of 23.7 % (acting as an Ohmic patch) and a 100-nm thick sputtered ITO film yielded a low specific contact resistance of ~1.3x10^{-2} Ωcm^2, a sheet resistance of 24 Ω/sq, and a high optical transmittance of 90 % at 450 nm. LEDs fabricated with the hybrid ITO TCEs showed a 17.2 % brighter light output power compared to reference LEDs. This indicates that the high-quality sputtered ITO film can be practically used in LEDs by embedding Pt nanoclusters.

EM-TuP16 Selective Area Growth of InN on Patterned Substrate by Plasma-Assisted Metal-Organic Molecular Beam Epitaxy

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In this article, we investigated selective area growth of InN materials on sapphire substrate using molybdenum mask patterned with various growth temperature. The surface morphology, structural and optical properties of InN materials were analyses by field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), X-ray diffractiometer and photoluminescence, respectively. XRD results indicated that the InN materials exhibited preferred orientation along the <0001> direction at 550 °C. Surface morphology shows that the InN crystals were grown on Mo-patterned substrate with *hexagonal* micro-rods *array* surface texturing. TEM images show these InN films are single phase wurtzite crystals with preferred orientation along the *c* axis. Optical properties showed the peaks of near band-edge emission at energies between 0.72 - 0.9 eV.

EM-TuP17 N+-InGaP or N+-GaAs NanoWires for JunctionLess Transistors Fabricated by Focused Ion Beam (FIB) System

***Cássio Almeida**, L.P.B. Lima,* UNICAMP, Brazil, *H.T. Obata, M. Cotta,* University of Campinas, Brazil, *J.A. Diniz*, UNICAMP, Brazil

N+-InGaP and N+-GaAs layers were grown by Chemical Beam Epitaxy (CBE) on GaAs substrates with (001) orientation. Two group of samples with N+-InGaP (350 nm)/GaAs-buffer layer (300 nm)/GaAs S.I. (Semi-Insulating) and N+-GaAs (300 nm)/GaAs-buffer layer (300 nm)/GaAs S.I. were obtained. X-Ray diffraction (XRD) analysis was used in order to determine the InGaP lattice mismatch on GaAs. N+-InGaP lattice-matched layers on GaAs were obtained using a growing temperature of 550°C during the process in CBE reactor, while, for N+-GaAs on GaAs samples, the temperature was 550°C. By Hall measurements, a silicon doping of 10^{+18} cm^{-3} was extracted for both group of samples, indicating the formation of N+-type layers. These samples are being used for MOS Junctionless (JL) Transistors applications, because III-V semiconductors present higher electron mobility values than silicon. These JL transistors (with three terminals: gate, source and drain) are being fabricated using Focused Ion Beam (FIB) System, based on similar process steps of the JL devices, which were fabricated on Silicon-on-Insulator (SOI) substrate[1]. Thus, Gallium (Ga$^+$) Focused Ion Beam (FIB) is used to define the III-V (InGaP or GaAs) nanowires (III-VNW), which are the electron conduction channel between source and drain, and for depositions of SiO$_2$ (as gate dielectric) and Pt (as gate, drain and source electrodes) layers[2]. Finally, drain-source current (I$_{DS}$) versus drain-source voltage (V$_{DS}$) and drain-source current (I$_{DS}$) versus gate-source voltage (V$_{GS}$) measurements of Junctionless devices will be extracted and will be able to indicate if these InGaP or GaAs nanowires are suitable for Junctionless transistors applications.

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EM-TuP18 Thermoelectric Figure of Merit of E-Beam-Grown Nanoscale Multilayered Bi$_2$Te$_3$/Sb$_2$Te$_3$ Thin Films

***Zhigang Xiao**, S. Budak*, Alabama A&M University

Nanoscale multilayered Bi$_2$Te$_3$/Sb$_2$Te$_3$ thin films were grown using the e-beam evaporation. The in-plane and cross-plane micro thermoelectric devices were fabricated using the clean room-based microfabrication techniques such as UV lithography. The e-beam-grown multilayered thin films and the fabricated thermoelectric devices were measured and characterized. The nanoscale multilayered Bi$_2$Te$_3$/Sb$_2$Te$_3$ thin films can have much higher thermoelectric figure of merit than their bulk materials. The measurement results on the electrical and thermal properties of the nanoscale multilayered thin films will be reported in the conference.

EM-TuP21 Band-Gap Measurements of Low-K Porous Organosilicate Dielectrics using Vacuum Ultraviolet Irradiation

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Porous low-k organosilicate dielectrics are of great interest in semiconductor fabrication due to their low-k properties and understanding their behavior during vacuum ultraviolet irradiation is important for their utilization in industry. Experimental measurements of the band-gap of low-k organosilicate dielectrics are presented in this work. Specifically, vacuum ultraviolet (VUV) synchrotron photoemission spectroscopy was used to investigate the effect of VUV radiation on porous organosilicate (SiCOH) dielectrics during processing. By comparing photoemission spectroscopic data before and after VUV exposure, VUV irradiation with photon energies less than 9.0 eV was found to be beneficial in depleting accumulated charge in SiCOH films while VUV photons with higher energies did not have this effect. Moreover, VUV irradiation with 8.9 eV photons depletes the most charge. This energy serves as a reference point from which other properties of the materials such as the location and presence of defect states could be detected and band-gap energy of SiCOH could be achieved finally. [1] In addition, a comparison of band-gap measurements of low-k dielectrics made with other techniques, such as X-ray photoelectron spectroscopy (XPS) [2] is presented.

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EM-TuP22 VUV Curing Process for Low-k Organosilicate Dielectrics

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Porous SiCOH films are of great interest in semiconductor fabrication due to their low-k properties. Post-deposition treatments of SiCOH thin films are required to decompose the labile pore generator (porogen) and ensure optimum network formation to improve the electrical and mechanical properties of low-k dielectrics. The currently used UV curing method has some weaknesses such as the required high curing temperature (400-425°C) and the time for curing (several minutes). Vacuum ultraviolet (VUV) irradiation over specific energy ranges was found to overcome some of these drawbacks by efficiently decreasing the dielectric constant and increasing the hardness and elastic modulus of low k dielectrics at room temperature. Specifically, photon energies equal to or larger than 6.0 eV were found to decrease the k value of SiCOH films while lower energies did not have this effect. 6.2 eV photons were found to be most effective. [1] In addition, photons with energies equal to or larger than 8.3 eV enhanced the mechanical properties of SiCOH films significantly. Fourier Transform Infra-red Spectroscopy (FTIR) shows that the breaking of C-H$_x$ stretching bonds (3050-2850 cm^{-1}) in organic porogens and transitioning of Si-O-Si stretching bonds (1250-1000 cm^{-1}) from cage-like to network-like structures contribute to the decrease of dielectric constant and increase of hardness and elastic modulus of SiCOH films. [2] [#_edn2] These investigations show that the optimum photon energies for post-deposition treatment of SiCOH might exist in the VUV range and a VUV-involved curing process could be utilized as a post treatment method in low-k material deposition technologies.

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EM-TuP26 Identification of Topological Surface States in $(Bi_{1-x}Sb_x)_2Te_3$ Thin Films, ***Jenna Walrath***, *A.S. Chang, V.A. Stoica, Y.H. Lin, W. Liu, L. Endicott, C. Uher, R. Clarke,* University of Michigan*, R.S. Goldman*, University of Michigan, Ann Arbor

Bi_2Te_3 and Sb_2Te_3 are well-known materials for thermoelectric applications, which have also recently been identified as topological insulators (Tis) with surface states consisting of a single Dirac cone. Spin-momentum locking in Tis make them desirable for spintronics and other applications. However, to be useful for such devices, these materials must be bulk insulating and have accessible surface states, requiring both the Fermi level and the Dirac point to be located within the bulk bandgap. Furthermore, it is desirable to possess these properties at room temperature in ambient conditions. Robust surface states in ambient conditions have been demonstrated for Bi_2Se_3, [1] but to our knowledge direct detection of topological surface states has yet to be demonstrated in BiSbTe systems. Here we use scanning tunneling microscopy and spectroscopy to characterize the band structure of 30nm MBE-grown $(Bi_{.42}Sb_{.58})_2Te_3$ thin films, revealing the presence of topological surface states within the bulk band gap. Both the Fermi level and the Dirac point are located inside the bulk bandgap, indicating bulk insulating behavior with accessible surface states. Furthermore, the surface states are robust to room temperature and limited air exposure.

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EM-TuP27 Quantitative Potential Profiling Across Metal-Oxide-Semiconductor Stacks, ***Sylvie Rangan***, *M. Kalyanikar, J. Duan, G. Liu, R.A. Bartynski, E. Andrei, L. Feldman, E. Garfunkel*, Rutgers, the State University of New Jersey

Band alignment between materials and potential changes across thin films is of great importance for understanding electronic properties of multilayer structures and their resulting properties in devices. Although energy alignment and band bending has been studied for decades, an accurate profile of the potential across an ultrathin insulating layer (<10nm) has yet to be determined. In this work, we have developed a new approach to precisely measure the potential profile across Metal/Oxide/Semiconductor (MOS) stacks under in-situ gate-biasing conditions, using x-ray photoemission spectroscopy (XPS). Previous attempts of potential profile measurements have been limited to qualitative assertions due to the absence of controlled biasing. Here, interface dipoles and band bending at the oxide/semiconductor interface, as well as the effective potential across the oxide have been directly measured as a function of the bias applied between the semiconductor and the gate. This technique opens a large field of research, as it allows simultaneously a chemical mapping and a quantitative characterization of potential profiles in novel structures.

Energy Frontiers Focus Topic
Room: Hall 3 - Session EN-TuP

Energy Frontiers Poster Session

EN-TuP1 Effect of Ultra-violet Light on the Degradation in Organic Solar Cells, ***Kenji Harafuji***, Ritsumeikan University, Japan*, H. Sato*, Ritsumeikan University

Organic solar cells (OSCs) offer many desirable properties such as flexibility, low cost, and easy fabrication. The lifetime is, however, still short. The degradation may be driven by light illumination, exposure to external air, and high temperature.

The degradation phenomenon under repetitive light illumination and high-vacuum is experimentally investigated in small molecular OSCs. The OSC has a structure of an indium tin oxide (anode)/copper phthalocyanine (donor, 20 nm)/fullerene (acceptor, 40 nm)/bathocuproine (buffer, 10 nm)/Ag (cathode, 100 nm). Xenon lamp illumination with an intensity of 100 mW/cm^2 is performed, and an air mass 1.5 global spectrum is obtained using a solar simulator. The repetitive illumination with the period of 30 s is composed of 100 repetitions of 3 s illumination followed by 27 s in the dark. The effect of light wavelength on the degradation is studied with the use of a long-pass filter of cut-wavelength λ_c. The filter allows the transmission of light into the OSC only with its wavelength longer than λ_c. Six kinds of filter with λ_c=0, 320, 370, 400, 550 and 665 nm are used.

It is found that the OSC degradation is dominated by the UV (ultra-violet) light with wavelength less than 400 nm. The short-circuit current density J_{sc}, open-circuit voltage V_{oc}, and fill factor FF in the case of λ_c=0 nm (without the filter) are decreased approximately 20%, 40%, and 60% compared with the case of λ_c greater than 400 nm at the 100th illumination, respectively. Resultantly, power conversion efficiency η_p is decreased 80%. The η_p value is decreased 60% with the filter of λ_c =320 nm, whereas initial η_p is almost kept even at 100th illumination with the filter of λ_c =400 nm. An S-shaped kink appears near the V_{oc} region in the current-voltage (J-V) characteristics at 100th illumination in the case of λ_c shorter than 400 nm. This shows the increase of series resistance in the OSC. The origin may be due to the disorder of crystal structure at the anode/donor interface. There are no appreciable changes of J-V characteristics between at 1st and 100th illuminations in the case of λ_c longer than 400 nm.

On the other hand, the initial η_p value at the first illumination is much smaller as λ_c is increased in the range of λ_c longer than 400 nm, accompanied by the large decrease of J_{sc}. This is because the total amount of light energy transmitted into active organic layers is decreased as λ_c is longer.

The origin of the degradation by illumination is revealed to be the UV light component with its wavelength shorter than 400 nm. The optimum λ_c value is 400 nm from the compromise between initial efficiency η_p and OSC degradation.

EN-TuP2 Characteristics of DSSC Fabricated at Low Temperature, ***EunChang Choi***, *J.U. Wie, B.Y. Hong*, Sungkyunkwan University, Republic of Korea

Dye-sensitized solar cells (DSSCs) have been widely investigated as a next-generation solar cell because of their simple structure and low manufacturing cost. To realize a commercially competitive technology of DSSCs, it is imperative to employ a technique to prepare nanocrystlline thin film on flexible organic substrate, aiming at increasing the flexibility and reducing the weight as well as the overall device thickness of DSSCs. The key operation of glass-to-plastic substrates conversion is to prepare mesoporous TiO2 thin film at low temperature with a high surface area for dye adsorption and a high degree of crystallinity for fast transport of electrons. However, the electron transport in the TiO2 film synthesized at low temperature is very poor. So, in this study, TiO2 films synthesized at high temperature were transferred on the selective substrate. We fabricated DSSCs at low temperature using this method. So, we confirmed that the performance of DSSCs using TiO2 films synthesized at high temperature was improved.

EN-TuP3 Conductivity Enhancement Effect of Sodium Dodecyl Sulfate on PEDOT:PSS for Organic Solar Cell Application, *K.-H. Hwang, H.J. Seo, S.-H. Nam, Y.J. Kim, C.Y. Park,* ***Jin-Hyo Boo***, Sungkyunkwan University, Republic of Korea

There are many researches on PEDOT:PSS treatment for application to flexible device electrode. Almost PEDOT:PSS treatment is consisted with step adding little bit surfactant to enhancement of adhesion between PEDOT:PSS and substrate or TCO materials. But basic research about surfactant effect is lacking. We study on the effects of sodium dodecyl sulfate (SDS) with controlling the concentration in aqueous PEDOT:PSS solution, and we confirm the conductivity enhancement of the mixture thin films with surfactant and PEDOT:PSS. Thin films are firstly prepared by spin coating method and then fabricated organic solar cells. To study the structural effects on the resulted electrical properties, thin films are mainly investigated by FE-SEM (Field Emission Scanning Electron Microscopy), AFM (Atomic Force Microscopy), respectively. At the same time, electric properties are also investigated by both 4-point probe and solar simulator.

Keywords: PEDOT, SDS, Surfactant, Organic solar cell, Electrical conductivity

EN-TuP4 Study of the Synthesis of Cu_2ZnSnS_4 Thin Films by Reactive Magnetron Co-Sputtering, *P.-A. Cormier,* ***Rony Snyders***, University of Mons, Belgium

Cu_2ZnSnS_4(CZTS) has attracted significant attention for thin film solar cells because it is composed on earth abundant and non-toxic elements and, has an optimal band gap of 1.5 eV. The control of the film stoichiometry is critical during the growth of CZTS thin films. We previously demonstrated the possibility to grow close to stoichiometric and phase pure crystallized CZTS thin films by reactive magnetron co-sputtering [1]. The films were close to stoichiometric (Zn/Sn=1.1-1.4, Cu/[Zn+Sn]=0.9-1.1). Nevertheless, it has been suggested that Cu-poor Zn-rich CZTS have would present the best solar cell performances [2].

Therefore, in the present work, aiming to better control the film stoichiometry and to deeper understand the relationship between the chemical composition of the deposited film and its phase constitution and ultimately to reach the best performances of the cell, two Cu poor CuSn targets presenting Cu/Sn ratio of 1.5 (CuSn1.5) and 1 (CuSn1) have been utilized. In both case, the effect of the sputtering power (P_{CuSn}) on the material properties has been studied. The films were characterized by multiwavelength Raman spectroscopy (785 and 325 nm), by X-Ray Diffraction (XRD), and by Energy-dispersive X-ray spectroscopy (EDX).

As expected, the phase constitution is affected by increasing P_{CuSn}. Using the CuSn1.5 target, its evolution is similar than the one observed using the CuSn2 target [1]: at low P_{CuSn}, the films mainly contain CZTS, with a low content of ZnS. Increasing the power, CZTS disappears to the profit of SnS, Cu_4Zn clusters, S_6 and ZnS. On the contrary, using the CuSn1 target does not allow the formation of CZTS dominated films. Indeed, even for the low P_{CuSn} conditions, ZnS dominates the Raman spectra. For medium power (P_{CuSn} = 45W), the film is composed by SnS, S_6, ZnS and CZTS while for higher powers, the films are similar than the one obtained with the CuSn1.5 and CuSn2 targets and the CZTS is replaced by Cu_4Zn clusters. For all sets of data, the concentration in Zn is stable. Therefore, the decomposition of the CZTS material seems to be related to the increase of the Cu and Sn concentrations and to the decrease of the S one, which deviates from the theoretical values in CZTS. Based on these data, a phase diagram can be built.

Finally, one film of each region was synthesized and used in solar cell devices in order to investigate the influence of the phase constitution on the cell performance with efficiency up to 1.8%.

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[2] Mitzi et al., Solar Energy Materials & Solar Cells 95 (2011)

EN-TuP5 Development of Low Cost, Solution Deposition Method for High Efficiency Cu_2ZnSn S_xSe_{4-x}(CZTSSe) Thin Film Solar Cells, ***Cheik Sana***, *S. Shahriar, J. Galindo, D. Kava, D.R. Hodges*, University of Texas at El Paso

Non-vacuum, solution based processing of earth abundant $Cu_2ZnSnS_xSe_{4-x}$ (CZTSSe) has attracted considerable interest as a material capable of driving economical and terawatt capacity photovoltaic module production. It has already shown promising results with solar cells efficiency up to 12.6%. The interest to CZTSSe as an absorber layer for thin film solar cells is due to its large absorption coefficient of over 10^4 cm^{-1} in the visible range, its tunable optical band on-vacuum solution based method to deposit $Cu_2ZnSnS_xSe_{4-x}$ (CZTSSe) was investigated. In this approach, a precursor solution of CZTSSe is formed by reacting metal sources copper (II) acetate monohydrate, zinc (II) acetate dehydrate, tin (II) chloride dehydrate and elemental powders of sulfur and selenium powders in a solution of 2-metoxyethanol. The slurry was then spincoated followed by annealing at different temperatures. Optical, structural and electronic characterization of thin films were performed using scanning electron microscope (SEM), X-ray diffractometer (XRD), raman spectrometer, UV-Vis spectrophotometer, 4 point probe and Hall Effect Measurement System. Film thickness was measured using Dektak 150 surface profilometer. X-Ray diffragtograms show different shifts of the kesterite/stannite (112) peak, which indicates the presence of CZTSSe. The three major peaks of the (1112, (220), and (312) planes had respective 2θ in the vicinity of 28°, 47.5° and 56°. The shift of the peaks depends on the ratios of S/Se in the synthetized material. The lattice constants decrease linearly with increasing contents of S in the precursor solution. Raman spectroscopy showed traces of both quaternary CZTS and CZTSe.

EN-TuP7 Synthesis and Characterization of Electron Beam Deposited $Cu_2ZnSn_{1-x}Si_xS_4$ Thin Films, ***Alejandro Alvarez Barragan***, *S. Exarhos, J. Hernandez, L. Mangolini*, University of California - Riverside

Nowadays, $Cu_2In_xGa_{1-x}Se_4$ (CIGS) and CdTe are the leading commercially available compounds in thin film photovoltaics technology. Nevertheless, the scarcity of In and Te, and the toxicity of Cd, are considerable threats that may hinder the production and increase the cost of these materials in the near future. Replacement of In, Ga, and Se in CIGS with Zn, Sn, and S yields the promising quaternary compound Cu_2ZnSnS_4 (CZTS). This material has a favorable direct band gap of 1.5 ev. Further, each of its constituent elements is earth abundant and non-toxic. These two attractive characteristics make it plausible to launch CZTS as the wave of the future in thin film PV. We now present the synthesis process of CZTS by electron beam evaporation and a subsequent sulfurization step[1]. A thin film of Zn, Cu, and Sn stacked layers was obtained upon localized heating of their respective metallic sources. The as-deposited layers were subsequently sulfurized under a vacuum inside a sealed quartz tube at temperatures ranging from 500°C to 600°C. One of the main difficulties that has been reported for CZTS synthesis is the stoichiometric control of the material. Secondary, unwanted phases such as CuS, SnS_2, ZnS, and Cu_2SnS_3 may nucleate if the initial atomic percentage of the layers or the sulfurization parameters are off a small window in which CZTS can be produced[2,3]. Extreme care was taken to prevent this issue. Characterization techniques such as Energy Dispersive Spectroscopy (EDS), X-ray Diffraction (XRD), and Raman Spectroscopy were heavily employed to confirm the presence of CZTS crystals. We are also presenting preliminary results regarding the synthesis of a $Cu_2ZnSn_{1-x}Si_xS_4$ structure. To the best of our knowledge, synthesis of this compound by the E-beam evaporation and sulfurization process is yet to be reported. Previous theoretical and experimental data regarding its wide band gap add up to the interest of engineering this material for optoelectronic applications[4].

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EN-TuP8 Optical and Photocatalytic Properties of Nanostructured Ce-TiO_2 Mixed Oxides, *R. Ramirez-Lopez,* Escuela Superior de Ingenieria Quimica e Industrias Extractivas-IPN, Mexico, ***Isaias Hernandez-Perez,*** Universidad Autonoma Metropolitana- Azcapotzalco, CBI, Mexico, *R. Suarez-Parra,* Instituto de Energias Renovables, UNAM, Mexico, *RT. Hernandez-Lopez,* Universidad Autonoma Metropolitana- Azcapotzalco, CBI, Mexico, *A. Garcia-Sotelo, E. Campos, M. Melendez-Lira*, Cinvestav-IPN, Mexico

The use of nano-crystalline TiO_2 is a promising strategy for photocatalytic remediation of wastewater due to its broad ability to remove various pollutants in aqueous media. In order to use a major part of the spectral solar distribution it would be necessary to reduce the bandgap of TiO_2 based materials. In this study, a series of nanocrystalline CeO_2-TiO_2 powders were successfully synthesized by sol-gel at room temperature, employing titanium isopropoxide and cerium nitrate as precursors, with nominal 2, 5, 10, 20 and 50 % of CeO_2:TiO_2 molar ratio. The crystalline structure, surface morphology and optical properties of synthesized samples were characterized using powder XRD, TEM, SEM, XPS. The optical band gap was determined by DR-UV-Vis spectroscopy and the emission spectrum by photoluminescence spectroscopy. Photocatalytic activity was evaluated by the photodegradation of Orange II azo dye, employing two different sources of irradiation 365 and 425 nm. Structural characterization showed that the Ce-TiO_2 particles crystallized into the anatase phase. TEM micrographies shown clearly the formation of nanocrystals. The optical bandgap energy shows a red shift for all synthesized samples compared with pure TiO_2. The results shown that the incorporation of 5 % CeO_2 effectively improves the photocatalytic activity comnpared wit pure TiO_2 at UV; while Ce incorporation activates it for 425 nm excitation still the nominal 5% shows the best performance. The results are discussed in terms of the electronic structure modification by Ce incorporation in the TiO2 matrix.

EN-TuP9 Hybrid Photoelectrode Based on Two-Dimensional Materials Decorated $BiFeO_3$ Thin Films for Efficient Solar Water Splitting, *C.M. Youn, H. Lee, J. Lee, H. Lee,* ***Taekjib Choi***, Sejong University, Republic of Korea

Semiconducting metal oxides have been attracted much interest as photoelectrodes for solar water splitting because of their stable photochemical activity in aqueous solutions. However, photoelectrochemical performance is usually limited by poor charge carrier separation. Thus, hybrid photoelectrodes combined with semiconducting ferroelectric materials offer promising potential for achieving efficient solar water splitting by promoting photogenerated-charge carrier separation due to spontaneous electric polarization leading to an increase in the elective electric field. In this study, we have fabricated two-dimensional materials decorated $BiFeO_3$ thin films as hybrid electrodes. The structural and optical properties of single and hybrid electrodes were comparatively characterized. The hybrid electrodes exhibited a stronger absorption of visible light and produced a higher photocurrent than that of single electrode. For hybrid electrodes, photoelectrochemical characterization demonstrated a large enhancement of the interfacial charge transfer kinetics as well as an efficient charge carrier separation, which greatly contributed to the improved photoelectrochemical performances. In addition, we will discuss poling effect of electric polarization on interface reduction/oxidation (REDOX) through electrolyte ions. Therefore, our results provide useful information for developing highly efficient hybrid photoelectrodes for solar water splitting.

EN-TuP11 Improvement in Photovoltaic Response of PLZT Thin Film Capacitors with ITO Electrodes, ***Sushma Kotru***, *V.N. Harshan, V. Batra*, The University of Alabama

Ferroelectric thin films of perovskite-type structure are of practical interest because of their excellent ferroelectric, dielectric and optical properties. Recently these materials have generated lot of research interest for photovoltaic applications (PV) . Photovoltaic properties of $Pb_{0.95}La_{0.05}Zr_{0.54}Ti_{0.46}O_3$ (PLZT) thin film capacitors prepared using solution based method with various top electrodes having different work functions are investigated. The results demonstrate that ITO (Sn doped In_2O_3), a transparent conducting oxide, as top electrode, enhances the magnitude of photo voltage and photo current as compared to metal electrodes. The photovoltaic efficiency is enhanced by orders of magnitude with ITO as top electrode when compared to metal electrode devices. Thus the choice of transparent conducting oxide as an electrode holds potential for improving the photovoltaic response of ferroelectric thin film capacitors.

EN-TuP14 Rational Design of Battery Architecture at Nanoscale: Self-Aligned Batteries Inside Nanopores via Atomic Layer Deposition, *C. Liu, E. Gillette,* ***Xinyi Chen****, A.J. Pearse, A.C. Kozen, M. Schroeder, K. Gregorczyk, S.B. Lee, G.W. Rubloff*, University of Maryland, College Park

A self-aligned nanostructured battery entirely confined within a single nanopore offers a powerful platform to investigate the rate performance and cyclability limits of nanostructured storage devices. Atomic layer deposition (ALD) has enabled such a structure that embeds coaxial nanotubular electrodes and electrolyte confined inside a single anodic aluminum oxide (AAO) nanopore, realizing an ultrasmall full cell battery with $\sim 1\mu m^3$ volume (~1fL). These nanopore batteries display exceptional power-energy performance and cyclability when tested as massively parallel devices ($\sim$2billion/cm^2). The extraordinary thickness and conformality control of ALD and the highly self-aligned nanoporous structure of AAO are crucial to fabrication of precise, self-aligned, regular nanopore batteries. Using controlled-conformality ALD processes, we optimized metal nanotube current collector (Ru or Pt) length at two ends of AAO nanopores to provide fast electron transport to overlying anode and cathode materials, while keeping them spatially and electrically isolated. Crystalline V_2O_5 was deposited as lithium ion storage material inside the metal nanotubes using O_3 as the oxidant. . Subsequently, the V_2O_5 was electrochemically prelithiated at one end to serve as anode while pristine V_2O_5 without Li at the other end served as cathode, enabling the battery to be cycled between 0.2V and 1.8V. Capacity retention of this full cell is 95% at 5C rate and 46% at 150C, with more than 1000 charge/discharge cycles. Further increase of full cell output potential is also demonstrated for SnO_2 and TiO_2 anodes in asymmetric full cells with V_2O_5 cathodes. These results reveal the potential of ultrasmall, self-aligned/regular, densely packed nanobattery structures as a building block for high performance energy storage systems and as a test bed to study ionics and electrodics at nanoscale with a variety of geometrical modifications.

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[1] Liu, C.; Gillette, E. I.; Chen, X.; Pearse, A. J.; Kozen, A. C.; Schroeder, M. A.; Gregorczyk, K. E.; Lee, S. B.; Rubloff, G. W., An all-in-one nanopore battery array. *Nature Nanotechnology* **2014,** *9* (12), 1031-1039.

In-Situ Spectroscopy and Microscopy Focus Topic
Room: Hall 3 - Session IS-TuP

In-Situ Spectroscopy and Microscopy Poster Session

IS-TuP1 Investigations of Graphene Covered Metal Catalyst using *Operando* Ambient Pressure X-ray Photoelectron Spectroscopy, ***Qiang Liu****,* Lawrence Berkeley National Laboratory (LBNL), *B.H. Mao,* Chinese Academy of Sciences*, E.J. Crumlin,* Lawrence Berkeley National Laboratory (LBNL)*, Z. Liu*, Chinese Academy of Science

Carbonaceous deposition is always observed in carbon-containing catalysis reactions on metal catalysts. This carbon deposition layer blocks the active sites of the metal catalyst and, therefore, inhibits the catalytic reaction. Recent research revealed that by depositing a graphene overlayer on metal catalyst the detrimental interaction between reactant gases and the metal catalysts can be weaken, thus resulting in a lowering of the activation energy barrier for the desired catalytic reaction. In order to probe the fundamental charge transfer processes between the as-grown graphene layer and the metal catalyst we present our studies of this system using *operando* ambient pressure X-ray Photoelectron Spectroscopy (APXPS), with synchrotron X-rays at the Advanced Light Source, Lawrence Berkeley National Laboratory. By intercalating gases (e.g. CO, O_2) quasi-free-standing graphene can be prepared, which annulled the charge transfer between as the as-grown graphene and the metal. Using APXPS, we have studied the graphene-reactant and reactant-metal interactions under different temperature and pressure conditions. We will discuss the results from graphene-Cu and graphene-CuNi system under CO oxidation reaction and other reaction conditions.

IS-TuP2 Probing the Electrode-Electrolyte Interfaces using *In Situ* Angle-resolved XPS, *V. Shutthanandan, M.I. Nandasiri, A. Schwarz, T.C. Kaspar,* Pacific Northwest National Laboratory*, S.A. Thevuthasan,* Qatar Environment and Energy Research Institute, Qatar*,* ***Murugesan Vijayakumar***, Pacific Northwest National Laboratory

The interaction between a charged surface (i.e. electrode) and an ionic solution (i.e. electrolyte) is the basic science that drives various systems ranging from biological membranes to energy storage and conversion devices. In a typical electrode-electrolyte interfacial region, ions from the electrolyte can form an electric-dipole with oppositely charged electrode and subsequently produce an electric double layer (EDL). This EDL formation is a highly reversible process that involves no chemical/phase changes and is widely used in modern devices such as chemical sensors, field-effect transistors and supercapacitors. However, a clear understating of the impact of the electrode surface chemistry and the nature of electrolyte ions on molecular structure-property relationship at modern interfaces is still lacking. One of the unique features of these interfaces is that they contain non-equilibrium ion concentration under biased conditions. A multilayer formation with alternative charges (*i.e.*, cation/anion) is expected under charged conditions, which can subsequently result in gradient change in ion concentration depend on the applied potential. To clearly distinguish the role of each electrode/electrolyte parameter under charging conditions, an unique *in-situ* angle-resolved X-ray photoelectron spectroscopy (AR-XPS) setup was developed at the Environmental Molecular Sciences Laboratory (EMSL) in Pacific Northwest National Laboratory. The change in composition of Ionic liquid electrolyte and specifically cation/anion ratio at different charging conditions was analyzed as a function of depth using *in-situ* AR-XPS. Preliminary results obtained from a model system consisted of porous carbon electrode and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquid electrolyte will be discussed here. In addition, the derived depth-profile information (such as surface adsorption and multilayer formation) will be compared with the number density profiles of cation/anions calculated from the optimized MD simulations.

IS-TuP3 Bimetallic Nanoparticles Stability Investigated by *In Situ* XPS and TEM, ***Cecile Bonifacio***, University of Pittsburgh*, S.C. Carenco, M.B. Salmeron,* Lawrence Berkeley National Laboratory*, J.C. Yang*, University of Pittsburgh

Bimetallic Ni and Co nanoparticles (NPs) possess intriguing potential for industrial applications due their remarkable catalytic activity for methane production and selective CO_2 reduction. Synthesizing these NPs as a core-shell structure presents a cost-effective way to produce catalysts by using the less expensive metal in the core and the more expensive but active metal catalyst in the shell. The core-shell structure can also allow for the fine tuning of reactivity, aversion of sintering issues for the core material, and even enhancement of tolerance to high temperatures. Unfortunately, NPs tend to be unstable at temperatures far below their bulk melting temperature. In this work, the structural stability of Ni-Co core-shell was studied using *in situ* techniques. The morphological, structural, and chemical changes involved in the core-shell reconfiguration were examined during *in situ* annealing through simultaneous imaging and acquisition of elemental maps in the transmission electron microscope (TEM), and acquisition of O 1s, Ni 3p, and Co 3p x-ray photoelectron spectra (XPS). By observing the structural rearrangements of the nanoparticles *in situ* as a function of temperature, we were able to determine the thermal conditions under which the as-synthesized structure is stable and the minimum temperature where significant elemental diffusion and aggregation occurs. The NPs were annealed *in situ* in the TEM and XPS from 80°C to 650°C under vacuum conditions. Energy-dispersive x-ray spectroscopy (EDS) maps were acquired after each annealing step, yielding the quantitative distribution of Ni and Co within the NPs. Our results show that core-shell reconfiguration occurred in a stepwise process of surface oxide removal and metal segregation. Removal of the stabilizing surface oxide occurred from 320°C to 440°C, initiating the core-shell reconfiguration. Above 440°C, Ni migration from the core to the shell disrupted the core-shell structure of the NP leading to the subsequent formation of a homogeneous Ni-Co mixed alloy at 600°C. This work impacts other fields besides catalysis – including metallurgy, magnetism, etc. – where nanoparticle stability under operating conditions is essential for their technical viability and long-term durability.

Materials Characterization in the Semiconductor Industry Focus Topic
Room: Hall 3 - Session MC-TuP

Materials Characterization in the Semiconductor Industry Poster Session (All areas)

MC-TuP1 Effect of Aromatic Compounds on Semiconducting Boron Carbide Heterojunctions, ***Elena Echeverria,*** University of Nebraska - Lincoln*, R. James, F. Pasquale, B. Dong,* University of North Texas*, A. Enders,* University of Nebraska - Lincoln*, A. Kelber,* University of North Texas*, P.A. Dowben*, University of Nebraska - Lincoln

A new class of semiconducting boron carbide devices was fabricated based on a carborane icosahedra ($B_{10}C_2H_{12}$) precursor via plasma enhanced chemical vapor deposition in the presence of aromatic linking units. Our studies have showed that these novel superconducting boron carbide films have excellent rectifying characteristics when deposited on n-type Si, making this heterojunctions extremely promising for neutron detection and other device applications. Films were fabricated by co-deposition of aromatic compounds (pyridine, benzene, diaminobenzene, etc.) with ortho-carborane using plasma enhanced chemical vapor deposition (PECVD). In the case of samples containing pyridine, the characteristic I–V curves for the heterojunction diodes exhibit strong rectification and largely unperturbed normalized reverse bias leakage currents with increasing pyridine content. Similar results are showed when benzene or diaminobenzene are used as linking groups, with a threshold voltage lower for diaminobenzene compared to benzene. These results suggest that modifications to boron carbide may result in better heterojunction diodes, and point the way to a whole family of future studies that may ultimately lead to boron carbides better suited to low power and low flux neutron detection.

MC-TuP2 3 Dimensional Quantitative Composition and Structure Profiling of As Implanted Si USJ and FINFET with TOF-MEIS, ***WonJa Min****, K.S. Park, K.-S. Yu,* KMAC, Republic of Korea*, S.J. Joo, Y.-S. Kim,* KRISS, Republic of Korea*, D.W. Moon*, DGIST, Republic of Korea

Using a recently developed time-of-flight (TOF) medium energy ion scattering spectrometer (MEIS), we have investigated 3D elemental composition, morphology, and atomic defect structures for As implanted Si ultrashallow junctions (USJs) and As implanted FINFET nanostructures.

As depth profiles in As/Si ultra shallow junctions (USJs) were measured by TOF-MEIS for 2 keV As implantation ion energy before and after annealing. Electrically inactive arsenic (As) complexes in silicon are investigated. In heavily As-doped Si, the As atoms segregated in the interface Si region just below the SiO_2 layer are found to be in interstitial forms (As_i), while the As in the bulk Si region are found to be in the substitutional form (As_{Si}). Despite the substitutional form of As, most of the As are found to be electrically inactive in the bulk region, and we identify that the As forms the <111> oriented As_{Si}-Si-vacancy (As_{Si}-V_{Si}) complex. The As_i's in the interface Si region are found to exist together with Si-interstitials (Si_i). It is suggested that the As_i deactivation centers in the interface Si region possibly accompany Si_i defects.

3D compostional distributions of As implanted FINFET structure were also analyzed with TOF-MEIS. Progresses in TOF-MEIS analysis of other nano-structured materials and devices in various nano & bio technology will be also discussed.

MC-TuP3 Characterization of the Doped Amorphous Carbon Hardmask Film Prepared by Hybrid Plasma CVD Systems, ***Jaeyoung Yang****, K.P. Park, G.H. Hur*, TES Co. Ltd., Republic of Korea

We investigated the single and laminated stacked doped amorphous carbon film with additive gas as boron and nitrogen, and so on. The film properties was characterized by XPS, SIMS, and FT-IR spectroscope. Boron doped carbon film with B concentration-had > 30 % had the highest selectivity to oxide of over 10:1. In this study we had a choice of hybrid plasma chemical vapor deposition (CVD), and it was very stable plasma condition for a long time process and the specified laminated stacked carbon hardmask films were consisted with nitrogen and boron. We considered our optimised doped carbon films can be applied to use as the hardmask for designing about photolithograph and etching process. We can be easily controlled to dopant ratio by the plasma deposition system with the pulsed source feed-through module. Our new hardmask material prepared by hybrid plasma CVD process will be candidate on future material for advanced logic and memories, including DRAM and 3D VNAND chip integration process. We introduced the several behavior of deposited film' properties with varying the deposition parameters into the hybrid plasma CVD systems.

MC-TuP4 Surface Structure and Morphology of GaAs Nanowires Grown by Aerotaxy*, **Sofie Yngman**, S. McKibbin, J. Knutsson, F. Yang, E. Lundgren, M. Magnusson, R. Timm, A. Mikkelsen*, Lund University, Sweden

III-V semiconductor nanowires (NWs) continue to show promising results as components in energy saving devices. GaAs NW arrays recently beat the record for photovoltaic solar cells presenting a conversion efficiency of 15.3% [1]. Given the large surface to volume ratio of NWs, performance in such devices may be strongly determined by surface characteristics for example, morphology, the presence of various oxide species and surface structure. We study GaAs NWs grown by using the novel growth technique aerotaxy [2]. In aerotaxy growth the NWs are catalyzed from Au aerosol nanoparticles floating freely in a continuous N_2 flow mixed with group III and V precursor gases. The growth rate of NWs using aerotaxy is much faster than for epitaxially grown NWs and the absence of expensive crystal substrate allows large scale economic production. A detailed understanding of the surface properties of these aerotaxy NWs is highly relevant in order to optimize device performance.

We compare surface structure and morphology of GaAs aerotaxy NWs to GaAs NWs grown epitaxially on a substrate. We obtain images of the NWs from microns to the atomic scale using both Atomic Force Microscopy (AFM) and Scanning Tunneling Microscopy (STM). Comparing this to chemical information obtained via X-ray Photoemission Spectroscopy (XPS) we find that the different growth techniques results in NWs with very different morphology. Using in air AFM phase measurements we show that the aerotaxy NWs exhibit a rounder cross section with few or no large facets in comparison to the hexagonal geometry of epitaxially grown NWs. XPS measurements show that by annealing the NWs in the presence of atomic hydrogen, we can remove the native oxides which form on them when exposed to air as previously observed for the expitaxially grown NWs[3][4]. From the XPS studies we can identify the different oxides present in the aerotaxy NWs before cleaning. We examine clean NWs using STM in Ultra High Vacuum. The morphology of the NWs is similar to as what is found in the AFM studies, however by direct atomic resolved imaging we can identify that even the round shaped aerotaxy NWs contain a considerable fraction of small unreconstructed patches of the {110} surface.

[1] http://www.solvoltaics.com/news.shtml (2015-05-01).

[2] M. Heurlin, et al. "Continuous gas-phase synthesis of nanowires with tunable properties", Nature 492, 90-94 (2012).

[3] E. Hilner, et al. "Direct atomic scale imaging of III-V nanowire surfaces", Nano Letters 8, 3978 (2008).

[4] M. Hjort, et al. "Direct imaging of atomic scale structure and electronic properties of GaAs wurtzite and zinc blende nanowire surfaces", Nano Letters 13, 4492 (2013).

MC-TuP5 Characterization of Si/Ru and Si/B_4C/Ru Multilayers using X-ray Reflectivity, X-ray Diffraction and Synchrotron-based EUV Reflectometry, ***Mohammad Faheem***, GLOBALFOUNDRIES Inc.*, P. van der Heide,* GLOBALFOUNDRIES, Inc.*, O. Wood, Y. Liang, A. Kumar Kambham, K. Wong, V. Park, P. Mangat*, GLOBALFOUNDRIES Inc.

Future photomasks for extreme ultra violet lithography (EUVL) would be improved with broader bandwidth reflective multilayer coatings especially below the 7 nm technology node. Owing to its lower index of refraction, higher numerical aperture and contamination resistance Ruthenium (Ru) is a potential candidate for use on future generation EUVL masks. We characterized 20 layer stacks of Si/La, Si/Ru and Si/B_4C/Ru on Si (100) substrates. X Ray Reflectivity (XRR) and Atom Probe Tomography (APT) were carried out on a Si/La stack for period comparison. Si/Ru and Si/B_4C/Ru were prepared for phase comparison using XRR and X Ray Diffraction (XRD). Four samples of Si/B_4C/Ru multilayers with less than 1 Å period difference were compared using synchrotron-based EUV reflectometry.

XRR measurements were carried out using a Bruker D8 Discover with Cu K-alpha (λ = 1.542 Å) and a scintillator detector. Measurements were made at small detector angles, 2θ = 0-10°. For texture and crystallite size, locked coupled scans were carried out using 0.2 mm beam slit and Lenxeye detector in 1D mode along 2θ = 10-110°. Bruker's Eva software was used to measure the peak positions and the ICDD PDF-4 data base was used to identify the Ru peaks. The APT measurements were performed by LEAP 4000X-Si instrument under UV laser illumination.

The result indicates the close agreement between XRR and APT for a 20 layer La/Si stack. XRR spectra of Si/Ru and Si/B_4C/Ru showed the multilayer period of ~ 7nm with sharp peaks which indicate the uniformity of deposited multilayers. Ru and B_4C showed polycrystalline behavior compared to amorphous Si. XRD results demonstrate that Ru layers tend to have (002) texture both in Si/Ru and Si/B_4C/Ru samples. Ru crystallite size in Si/Ru was observed to be larger than in Si/B_4C/Ru. The difference in crystallite size can be due Ru film thickness and its deposition on Si and

B_4C. In the case of four Si/B_4C/Ru samples, the change in period was found to be correlated to changes in bandwidth and shifts in the position of peak EUV reflectivity. These results are not only of fundamental importance but also beneficial for improving the performance of Ru-based EUVL reflectors.

Key words: EUVL, XRR, XRD, APT, Synchrotron

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Magnetic Interfaces and Nanostructures
Room: Hall 3 - Session MI-TuP

Magnetic Interfaces Poster Session

MI-TuP1 Optical and Magneto-Optical Properties of Zn$_{1-x}$Mn$_x$O / ZnO Hollow Nanospheres, ***Da-Ren Liu***, *C.J. Weng*, National Applied Research Laboratories, Taiwan, Republic of China

Recently, diluted magnetic semiconductors (DMS) have generated widespread interest due to their potential applications for spintronic devices. Mn-doped ZnO is one of the most promising diluted magnetic semiconductors materials due to its room temperature ferromagnetism. In this study, ZnO layer was conformally deposited on the surface of polystyrene (PS) nanoshpere with different diameter (100nm~800nm) by atomic layer deposition (ALD). Then the Zn$_{1-x}$Mn$_x$O ($0 < x < 0.1$) coatings were grown on ZnO hollow nanospheres by pulsed laser deposition(PLD). According to the results of high-resolution x-ray diffraction, Mn-doping does not change the wurtzite structure of ZnO and the Zn$_{1-x}$Mn$_x$O hollow nanospheres are polycrystalline. Photoluminescence spectra and transmittance show an increase of the band gap with the increasing Mn ion concentration. The magneto-optical properties of the Zn$_{1-x}$Mn$_x$O / ZnO hollow nanospheres were measured by micro-MOKE spectroscopy and strongly depend on the Mn composition fraction.

MI-TuP3 Scanning Tunneling Microscopy Study of Magnetic Layers Grown on MgO(001) by Molecular Beam Epitaxy, ***Jeongihm Pak***, *A.-O. Mandru, J.P. Corbett, A.R. Smith*, Ohio University

Magnetic coupling between ferromagnetic (FM) and antiferromagnetic (aFM) layers is of high importance to exchange bias and related magnetic technologies. It is essential to achieve atomically smooth and flat magnetic films onto which we can deposit transition metals (e.g. Fe, Mn and Cr) to create magnetic bi-layer systems that will allow us to probe possible magnetic coupling. In this study, we grow FM Fe and aFM Mn and Cr films on MgO(001) using molecular beam epitaxy (MBE) and investigate the surfaces using scanning tunneling microscopy (STM).

The growth experiments take place in an ultra-high vacuum (UHV)-MBE chamber, equipped with Fe, Mn and Cr effusion cells, a 20 keV reflection high energy electron diffraction (RHEED), and a quartz crystal sensor (for flux calibrations). Fe, Mn and Cr films are grown on MgO(001) over a range of sample temperatures. The prepared samples are transferred *in-situ* to the adjacent UHV room temperature STM analysis chamber for surface studies. The streaky RHEED patterns indicate single crystal films grown with smooth surfaces and STM topography images reveal atomically smooth and flat surfaces on each film. X-ray diffraction (XRD) confirms the (001) growth face for Fe and Cr. Magnetic force microscopy (MFM) is performed on each film to explore the magnetic domain structure. Ultimately, we aim to extend the present study to include spin-polarized STM measurements that will probe the magnetic coupling between FM and aFM layers, e.g. sub-monolayer Fe on Mn (or Cr) substrates (and vice versa).

Manufacturing Science and Technology
Room: Hall 3 - Session MS-TuP

Aspects of Manufacturing Science and Technology Poster Session

MS-TuP1 Development of Graphene/Al Composite Materials with High Strength, ***Yusuke Oguro***, *A. Matsumuro*, Aichi Institute of Technology, Japan

Graphene shows many extraordinary properties. It is conducts heat and electricity with great efficiency and is nearly transparent. Furthermore it has the surprisingly mechanical properties with tensile strength of 100 times stronger than steel by weight and Young's modulus with 1 TPa. Now the field of the electronic device is studied energetically. But, studies are hardly investigated in the field of the application to new composite materials. The properties show superior high specific strength. We are convinced that they greatly contribute to develop the innovative materials and overcome environmental problem.

In this study, we focused on graphene/Al composite bulk materials. As graphene materials, we used nanographene with a several layers due to large quantity production and very cheap. Firstly we investigated the method of synthesis of monolayer nanographene sheet by our original ultrasonic vibration method in order to utilize original high strength characteristics of monolayer graphene sheet. We must also prevent from aggregation of graphene sheets in composite materials because the aggregation parts would surely cause a loss of strength of the materials. In order to disperse graphene around Al powders with average diameter of Al about 100 nm, the same ultrasonic vibration method was applied with isopropyl alcohol as a solvent before sintering composite materials . The powder before press sintering was prepared to dry in a furnace at about 340 K for 40 minutes. The composite materials with uniform dispersion of graphene were fabricated by with piston-cylinder type press apparatus under the condition of the applied pressure of 1 GPa and the temperature of 723 K for 4 hours in Ar gas atmosphere. We investigated the optimal condition of the composite materials as changing dispersion time by ultrasonic vibration from 1 to 6 hours. And we also investigated the optimal condition of the composite materials as changing composition rates from 0 to 3.0 wt.%graphene.

In our results, all composite materials sintered showed uniform bulk materials without aggregation of graphene. X-ray diffraction showed no metallic compounds between Al and nanographene. The densities of composite materials decreased down to 2.43 g/cm^3 of 3.0 wt.%graphene. Vickers hardness of the composite material at 1.0 wt.%graphene showed the maximum value of 308 Hv, and the density was 2.46 g/cm^3. So, the specific strength increased up to 396 kN・m/kg. It is about 1.4 times bigger than that of Al material. Therefore, graphene/Al composite materials give us dreams of development for innovative materials.

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 $5.5x10^{-5}$ 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 (5x10^{-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 90^{o}C. 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 NH_4OH 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 (NH_4OH) solutions (concentration of 9% wt) are used to get SiNWs and SiSMWs, because also these solutions are silicon orientation-dependent wet etching. Furthermore, NH_4OH 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 SiO_2 layer was grown using thermal oxidation. Lithography, SiO_2 etching (using HF solution) and organic cleaning (to remove photoresist) steps were carried out to define lines of SiO_2 (masking oxide) with width of 3 μm and spacing of 7 μm between lines. Reactive Ion Etching with SF_6 plasma was carried out, resulting in silicon three-dimensional (3D) mesa structures under SiO_2 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 NH_4OH 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 SiO_2 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 SiO_2 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 NH_4OH 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 SiO_2 of <110> plane 3D mesa sidewalls of 110 nm/min was repeated and SiNWs and SiSMWs were obtained, indicating that our NH_4OH 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.

Advanced Surface Engineering
Room: Hall 3 - Session SE-TuP

Advanced Surface Engineering Poster Session

SE-TuP1 Surface and Tribological Properties of CFx-doped TaN Thin Films With and Without CFx Top Layer, *W.C. Say,* ***ShangLun Liu,*** National Taipei University of Technology, Taiwan, Republic of China, *J.H. Hsieh*, Ming Chi University of Technology, Taiwan, Republic of China

TaN thin film coatings are known to have good mechanical properties, impact toughness, as well as good biocompactibility. However, the friction coefficient of these films is sometimes too high, or the hemocompatibility is poor. The purpose of this study is to reduce the friction coefficient and lower the surface energy of TaN coating by introducing CF_x into/onto the nitride coatings. CF_x–doped TaN films, with and without CF_x top layer, were deposited on silicon and tool steel substrates by magnetron sputtering. During the deposition process, C_2F_6 gas with various flow rates was added. During the deposition of 30 nm CF_x top layer on some samples, the power to Ta target was shut off. After deposition, these films were then characterized using XRD, XPS, FTIR, FESEM, as well as a tribometer. The tribo-tests were carried out with and without argon flow. Surface energies of the films were also analyzed with contact angle measurement system. According to structural analysis, TaN phase would transform to Ta(FCN) with the increase of the fluoride gas flow rate, which would cause the decrease of friction coefficient and surface energy. According to the results obtained from tribotesting, it is found the increase of CFx would reduce the effects of moisture and oxygen on friction coefficient. The prepared films may have good hemocompatibility and wear-resistance.

SE-TuP2 Biocompatibility of Porous TaOxNy Films with Various O/N Ratio

J.H. Hsieh, ***YiChih Lin***, *S.J. Liao,* Ming Chi University of Technology, Taiwan, Republic of China*, C. Li,* National Yang Ming University, Taiwan, Republic of China*, Y.H. Lai*, Ming Chi University of Technology, Taiwan, Republic of China

The oxynitride of a transition metal is able to form a new grade of functional thin film. Controlling oxygen-to-nitrogen ratio allows one to tune the film properties. The tunable properties include optical and mechanical properties, and biocompatibility, etc. In this study, TaOxNy-Cu films were first prepared using reactive co-sputtering, with the variation of O/N flow ratios. After deposition, the films were annealed, and Cu was etched away to form porous oxynitride structures with various O/N ratio. The films were characterized using nano-indentation, XRD, and SEM. The results showed that the porosity of these films could be varied depending on Cu contents and O/N ratios. The samples were then tested for their biocompatibility and viability using 3-T-3 fibroblast cells. According to the results obtained from biocompatibility and MTT assay testing, it was found that the O/N ratio should be near the transition of semiconductor to conductor. Furthermore, the pore size played a major role in terms of biocompatibility and cell viability. An optimal pore size was found around 200 um.

SE-TuP3 Nanopatterned ZnO on PDMS via Decoupled Ion Beam Modification and Metal Co-Deposition

Zachariah Koyn, *B. Holybee, A. Shetty, K. Nash, J. Pachicano,* University of Illinois at Urbana-Champaign*, S. Srivastava,* Illinois Applied Research Institute*, J.P. Allain*, University of Illinois at Urbana-Champaign

Ion beams have been shown to create nano-scale surface patterning on polycrystalline thin metal films, including ripples and dots [1,2]. Additionally, oxygen ion beams have been shown to induce fluence-dependent surface oxidation on metal surfaces [3]. This work seeks to unravel the directed irradiation synthesis of metal oxide thin-films, specifically ZnO, with irradiation-driven mechanisms on dissimilar, polymer-based substrates. This examines the dual effects of oxygen irradiation as a method of both oxidizing and patterning metal thin-films at ambient temperatures. This represents a scalable process in growing and functionalizing metal-oxide thin-films on polymers, which are sensitive to the high temperatures required in thermal oxidation processes. Recent work utilized a single ion beam to simultaneous irradiate and sputter deposit metal impurities on Si, creating nanostructures [4]. The work here decouples these processes by using two ion beams to independently control the metal deposition and surface modification fluxes. The ratio of these is the primary tool used to explore the creation and control over size and shape of nanostructures. Beam energies of 100-2000 eV are used at ambient temperatures to protect the substrate, with an inert beam used for metal deposition and both inert and reactive (O_2^+) normal incidence beams used for surface modification. Both Si and PDMS substrates are explored with fluences of ~5E16–2E17 ions/cm^2. Surface patterning and chemistry are analyzed with AFM and XPS, respectively. The ability to functionalize flexible, transparent substrates with metal-oxide nanostructures offers exciting applications in areas such as flexible and wearable electronics, gas sensors, biosensors, and photonics [5].

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SE-TuP4 Investigation of Tungsten-YttriumBased Structural Materials for Nuclear Reactor Applications

Gustavo Martinez, *J. Chessa,* University of Texas at El Paso, *M. Lerche,* Mcclellan Nuclear Research Center*, R.V. Chintalapalle*, University of Texas at El Paso

Material failure is one of the most considerable setbacks needed to be addressed by the materials research community to develop the next generation of nuclear energy systems that demand materials to serve under extreme conditions. We report on the enhanced irradiation tolerance and phase stability of nanocrystalline Tungsten-Yttrium (W-Y) coatings produced by radio-frequency sputter deposition. The W-Y coatings were produced under variable sputtering pressure and Y-content. The coatings were characterized by studying their structure and mechanical properties. The W-Y coatings were then subjected to heavy ion-irradiation at high fluence levels. The addition of Y atoms into the W matrix has shown to improve the irradiation bombardment of heavy Au+3 and yielding improved young's modulus and hardness when compared to pure W alone. It is believed that the addition of Y creates grain boundaries that are capturing interstitial ions and recombining to eliminate vacancies. The results will be presented and discussed.

SE-TuP6 The Influence of Mo Content and Bias Potential on the Structure, Mechanical Properties, and Tribological Behaviour of Cathodic Arc Evaporated Ti-Al-N Hard Coatings

Stefan A. Glatz, TU Wien, Austria*, C.M. Koller, H. Riedl*, CDL AOS, TU Wien, Austria*, R. Rachbauer,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*, S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*, P.H. Mayrhofer*, CDL AOS, TU Wien, Austria

Today's industrial processes, i.e. forming and shaping of various materials, require efficiency and precision. Therefore, wear and friction are core topics in the continuous improvement process. Coating either one of the counter-bodies or both of them with, for example, Ti-Al-N can be a feasible solution for fitting these certain requirements of the tribological conditions within industrial processes. Powder metallurgical manufacturing is ideal to produce materials with a broad composition and/or to alloy further elements to a standard target composition—i.e. to alter the properties of $Ti_{1-x}Al_xN$ thin films. This study focuses on the influence of bias potential and alloying element content on phase formation, mechanical properties, and tribological behaviour of cathodic arc evaporated $(Ti_{0.5}Al_{0.5})_{1-x}Mo_xN$ hard protective coatings. The tribological behaviour of the coatings obtained by using this physical vapour deposition (PVD) technique were evaluated by means of pin-on-disc tests and by non-contact optical profilometry—where the development of the wear tracks and counter-bodies is investigated. Scanning electron microscopy in combination with energy dispersive x-ray spectroscopy and x-ray diffraction experiments are performed to establish the chemical and structure evolution of our $(Ti_{0.5}Al_{0.5})_{1-x}Mo_xN$ thin films deposited with various bias potentials. It can be shown that the tribological behaviour of Ti-Al-N coatings can significantly be enhanced by the development of $(Ti_{0.5}Al_{0.5})_{1-x}Mo_xN$ thin films.

SE-TuP7 High-temperature Tribological Investigations of CrAlN and CrAlSiN in Ambient and Inert Atmospheres

Marisa Rebelo de Figueiredo, *A. Xia,* Montanuniversität Leoben, Austria*, S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*, R. Franz*, Montanuniversität Leoben, Austria

CrAlN-based hard coatings are nowadays widely used in industrial cutting applications to protect the base material of the tools against wear and oxidation. Due to alloying of the binary CrN with Al, enhanced mechanical properties of CrAlN could be achieved as a result of solid solution hardening, if the face-centered cubic structure of CrN is retained, i.e. Al atoms substitute Cr in the crystal lattice. An improved oxidation resistance is based on the formation of thin oxide layers on the coating's surface hindering further oxidation. With the addition of Si, a nanocomposite of crystalline CrAl(Si)N grains and an amorphous SiNx grain boundary phase can be formed resulting in a further enhancement of the mechanical properties. The oxidation resistance could also be further improved due to the formation of an additional SiOx phase on the coating surface. The tribological properties of these coatings at high temperature have already been studied in detail [1, 2]. However, these experiments were performed in ambient atmosphere impeding a clear identification of the main wear mechanism like abrasive or oxidative wear. Even though CrAlN and CrAlSiN are oxidation resistant at the test temperatures up to 700 °C, oxidation in the tribological contact zone might still play an important role if the protective oxide layer on the surface is removed and freshly exposed coating material can rapidly oxidize.

Therefore, CrAlN and CrAlSiN coatings were analyzed in ball-on-disk tests in ambient and inert Ar (+ N_2) atmosphere at temperatures ranging from room temperature up to 700 °C. The coatings were synthesized by DC magnetron sputter deposition in an industrial-scale system using composite $Cr_{50}Al_{50}$ and $Cr_{45}Al_{45}Si_{10}$ targets. The tribological tests against alumina counterparts revealed a coefficient of friction independent of the used atmosphere. The wear coefficient as determined by 3D optical profilometry, however, showed a non-uniform behavior. At medium temperature of about 400 °C higher wear in inert than oxidative atmosphere was noticed, whereas the opposite trend was observed at high temperatures of up to 700 °C. A subsequent analysis of the wear scars and the wear debris by scanning electron microscopy and Raman spectroscopy revealed further details about the wear mechanisms.

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Surface Science
Room: Hall 3 - Session SS-TuP

Surface Science Poster Session

SS-TuP1 Self-assembly and Thermally induced Conformational Changes of Ni(II)-*meso*-tetrakis (4-tert-butylphenyl) benzoporphyrin on Cu(111) Studied by STM, *Michael Lepper, M. Stark, L. Zhang,* FAU Erlangen-Nürnberg*, H.-P. Steinrück,* FAU Erlangen-Nürnberg, Germany*, H. Marbach*, FAU Erlangen-Nürnberg

A detailed scanning tunneling microscopy study of the self-assembly and thermally induced conformational changes of Ni(II)-meso-tetrakis (4-tert-butylphenyl) benzoporphyrin (Ni-TTBPBP) on Cu(111) will be presented. The coverage-dependent adsorption behavior at room temperature reveals that Ni-TTBPBP molecules can easily diffuse on the surface and self-assemble into islands with square order and a certain registry to the substrate.[1] The role of molecule-molecule and molecule-substrate interactions for the formation of the well-ordered supramolecular structure will be discussed. Interestingly, upon moderate heating two successive, irreversible intramolecular conformational changes are observed. This is explained comprehensively by a thermally induced dehydrogenative, intramolecular aryl-aryl coupling reaction. In addition this intramolecular structural change is coverage dependent, exhibiting a lower rate at higher initial coverage. This modification and the overall adsorption behavior of Ni-TTBPBP on Cu(111) will be discussed and compared to the very different behavior of the similar Ni(II)-tetraphenylbenzoporphyrin on the same substrate.

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SS-TuP3 Characterization of Pt-Re Bimetallic Clusters on $TiO_2(110)$, *Randima Galhenage, K. Xie,* University of South Carolina*, H. Yan,* Brookhaven National Laboratory*, G. Seuser, D.A. Chen*, University of South Carolina

The study of metal clusters on single-crystal oxide supports as model systems has garnered much attention for fundamental investigations of catalytically active surfaces that can guide the rational design of new catalysts. For instance, Pt-based catalysts have been recently proposed for the aqueous phase reforming of alcohols but suffer from a lack of stability due to poisoning by CO and other carbonaceous species. The addition of a second metal, such as Re, to Pt has been shown to increase the stability and the activity of the catalyst, but the exact reason behind this enhanced activity is not well understood. To better understand this bimetallic system, we have prepared model catalysts consisting of bimetallic Pt-Re clusters on TiO_2 to investigate the growth of metals, metal-metal interactions, metal-support interactions and activity using Scanning Tunneling Microscopy (STM), X-ray Photoelectron Spectroscopy (XPS), Low Energy Ion Scattering Spectroscopy (LEIS) and Temperature Programmed Desorption (TPD). Re shows strong metal support interactions (SMSI) even at room temperature, resulting in highly dispersed 2D clusters. Encapsulation of Re by TiO_x was observed due to SMSI effects. Pt-Re bimetallic clusters were prepared by depositing the less mobile Re first followed by deposition of Pt for submonolayer coverages. The surface composition of the bimetallic clusters was Pt-rich due to the lower surface free energy of Pt and the oxophillic nature of Re. CO adsorption behavior of the bimetallic clusters resembled the activity of pure Pt. At higher coverages (3.7 ML total metal coverage) bimetallic clusters were formed by both orders of deposition, Re on Pt and Pt on Re. When Re was deposited first, it resulted in a higher nucleation density for the bimetallic clusters with 100% Pt at the surface, and the activity resembled that of pure Pt. When Pt was deposited first, the initial seed cluster density was low, resulting in a lower density of bimetallic clusters, which led to a smaller number of active sites. In this order of deposition, the surface composition was a mixture of Pt and Re, and the activity studies suggest that both Pt and Re are active sites for the adsorption of CO. Pt-Re interactions were observed when Pt was deposited on titania followed by the deposition of Re.

SS-TuP4 Growth of Polymer Nanoparticles by Vapor Phase Polymerization onto Liquid Substrates, *Robert Frank-Finney, P. Haller, M. Gupta*, University of Southern California

The vapor phase deposition of polymers onto liquid substrates can result in the formation of polymer films or particles at the liquid–vapor interface. The initial polymer morphology at the interface is determined by the surface tension interaction between the liquid and polymer. Polymer particles form when it is energetically favorable for the polymer to aggregate rather than spread over the surface of the liquid as characterized by a spreading coefficient. The particles that are formed on the surface either remain partially protruding from the surface or submerge below the surface based on the engulfment energy of the polymer-liquid interaction. We systematically study the effects of deposition time, molecular weight, polymer accumulation, and liquid viscosity on the particle size and distribution to determine the mechanism of growth. Our results provide a fundamental understanding about polymer growth at the liquid–vapor interface that can be used to tailor the reaction conditions to produce particles of a desired size and improve upon the size distribution and can even offer insight into the growth of other materials on liquid surfaces. Vapor phase deposition onto liquid substrates is a rapid, one-step synthetic approach for fabricating functional polymer nanoparticles without the use of surfactants or volatile solvents.

SS-TuP6 Efficiency Improvement of $Cu_2O/NiO/TiO_2$ Solar Cells Prepared by Reactive Magnetron Sputtering, *Tomokazu Tsuchiya, I. Takano*, Kogakuin University, Japan

As one solution to the power shortage and global warming, a renewable energy such as solar cells is desired. Furthermore the high purity silicon that is the main raw material for solar cells is insufficient worldwide, and so new solar cells without silicon that are able to be replaced to silicon-based solar cells have been required. Practical application of oxide-based thin film solar cells is expected in reduction of the energy cost or the environmental load.

Generally a typical oxide-based thin film solar cell is a wet dye-sensitized solar cell composed of an electrolyte, an electrode of a titanium oxide and a sensitizing dye. Recently a solid-state dye-sensitized solar cell which uses metal oxides instead of an electrolyte has been studied. In our previous study on TiO_2/Cu_2O solid-state dye-sensitized solar cells, the main problem was Cu diffusion from the under layer Cu_2O. The diffusion of Cu to a titanium oxide layer induced the collapse of p-n junction.

The NiO thin film is used as a transparent oxide semiconductor. Most of the transparent oxide semiconductors are an n-type semiconductor, while NiO is a p-type semiconductor. In this study, we used NiO as a barrier layer between TiO_2 and Cu_2O for preventing the diffusion of Cu, and we investigated the characteristics of $Cu_2O/NiO/TiO_2$ solar cells.

$Cu_2O/NiO/TiO_2$ solar cells were fabricated by reactive magnetron sputtering. As substrates, the glass (Corning#1737) and an ITO-film coated glass were ultrasonically cleaned by acetone. The NiO thin film was deposited on those substrates by using pure metallic nickel (99.99%) as a sputtering target material in an oxygen gas atmosphere. The flow rate of an argon gas for sputtering was 20 sccm. The flow rate of an oxygen gas was 2.7 sccm. A thickness of the NiO layer was changed from 2 nm to 50 nm. On the other hand the fundamental preparations of the Cu_2O layer and the TiO_2 layer were performed by 200 nm in a thickness through 15 sccm and 20 sccm in an argon gas, and 10 sccm and 2.3 sccm in an oxygen gas, respectively.

$Cu_2O/NiO/TiO_2$ solar cells were successfully fabricated by reactive magnetron sputtering. The solar cell with the NiO layer of 4 nm thickness showed the maximum conversion efficiency of 5.6×10^{-3} % which was 9 times compared with the sample without the NiO layer.

SS-TuP7 Electrical Conductivity Control of Metal Doped DLC Films Prepared by N_2^+ Ion Beam Assistance, *Tsuyoshi Inoue, I. Takano*, Kogakuin University, Japan

DLC is amorphous carbon that contains a significant fraction of sp^2 and sp^3 bonds. It is known that their films show a low friction coefficient and are applied in a mechanical field such as cutting tools or frictional parts. DLC films were formed by the ion beam evaporation method in the early 1970's, and after that have been manufactured by various methods. In our experiment N_2^+ ion beam was used with metal evaporation to deposit metal doped DLC films. This deposition method has some independent parameters from the film formation condition in comparison with other dry process methods. Therefore this method is anticipated in appearance of superior characteristics such as a high adhesion. In our previous research, DLC thin films have been prepared by the N_2^+ ion beam assistance in a hydrocarbon gas. Their results showed that the films contained nitrogen of 8 % and mechanical properties were improved in hardness, friction and abrasion. On the other hand the electrical conductivity of metal doped DLC films prepared by this method is not clear.

In this study, the control of the electrical conductivity of DLC thin films was performed by the metal dope. Stainless steels (304SS) and slide glasses were used for sample substrates. The formation conditions of metal doped DLC films were changed with a metal evaporation rate from 0.01 nm/s to 0.05 nm/s and were an ultimate pressure of $6x10^{-4}$ Pa, an N_2 gas pressure of $4x10^{-3}$ Pa, a C_7H_8+N_2 gas pressure of $2x10^{-2}$ Pa in an ambient atmosphere. The ion beam irradiation was performed with 12 kV in an accelerating voltage and 5 $\mu A/cm^2$ in a current density, through an exposure time of 3600 s. The electrical conductivity and friction coefficient were determined by the four probe method and the tribotester of a ball-on-disk type, respectively. The tribotester was set with the conditions of an SUJ2 ball as a counter material and a constant load of 0.19 N until a sliding distance of 100 m.

The suitable electrical conductivity and mechanical property of the Ti or Cu doped DLC films were obtained by a Ti evaporation rate of 0.03 nm/s and a Cu evaporation rate of 0.05 nm/s respectively. The friction coefficient of Ti or Cu metal doped DLC films was about 0.24 - 0.23 at a distance of 100m. The electrical conductivity was 1.4×10^5 S/m in Ti doping and 5.17×10^6 S/m in Cu doping in comparison with the typical DLC film showing 1.0×10^{-7} S/m.

SS-TuP8 NEXAFS Studies of N_2O-N_2 Conversion on Reduced Ceria Surface, ***Alexei Nefedov***, *C. Yang, F. Bebensee, C. Wöll*, Karlsruhe Institute of Technology, Germany

Ceria, one of the most reducible metal oxides, has proven to be a highly active catalyst for NO_x reduction to N_2. Here, we use synchrotron based photoemission spectroscopy (PES) and near edge X-ray absorption fine structure spectroscopy (NEXAFS) to monitor the conversion of N_2O to N_2 over reduced ceria surfaces ($N_2O + CeO_{2-x} \rightarrow N_2 + CeO_2$) in a time-resolved fashion. This enables us to determine the kinetics of this process.

The NEXAFS and PES measurements were carried out using the HE-SGM beamline at the synchrotron facility BESSY II operated by the Helmholtz-Zentrum Berlin. The clean and stoichiometric $CeO_2(111)$ single crystal was annealed at 800 K for 15 min in vacuum to create surface oxygen vacancies prior to exposure to N_2O, whereas ceria powders were annealed at 1000 K for 30 min. Exposure to 50 Langmuir N_2O at sample temperatures typically below 120 K was achieved by backfilling the analysis chamber up to 10^{-9} mbar before NEXAFS spectra acquisition. The NEXAFS spectra were recorded in the partial electron yield mode for the π^* resonance region of N K absorption edge. The Ce oxidation state was judged by PES before and after N_2O exposure.

In the NEXAFS spectra, two intense resonances (401.2 eV and 404.8 eV) are observed. The resonances are assigned to the transition from the 1s orbital into the lowest unoccupied molecular orbital ($3\pi^*$) of the terminal and central nitrogen atom of N_2O, respectively. In agreement with previous experimental spectra for N_2O on $CeO_2(111)$ thin films, both resonances exhibit equal intensity. Theoretical calculations for thin films indicate that N_2O is adsorbed with the oxygen-end towards a cation on the surface also on the CeO_2 single crystal. Moreover, these two resonances decrease in parallel over time and one may speculate at this point that the decrease is caused by conversion of N_2O to N_2 over reduced $CeO_2(111)$. The difference in valence band photoemission spectra measured before and after the introduction of 50 Langmuir N_2O clearly demonstrate that the initial reduced $CeO_2(111)$ surface is re-oxidized to some extent and thus confirms the speculation above that N_2O can interact with oxygen vacancies resulting in vacancy healing.

Annealing can easily reduce ceria, while N_2O can heal the oxygen vacancies on the reduced ceria surface, giving rise to a complete catalytic cycle. The first set of data on N_2O adsorption and reaction over ceria surface suggest the feasibility of the study of the conversion of N_2O to N_2 by using PES and NEXAFS, which gives us a chance to determine the kinetics of this reaction.

SS-TuP9 Photocatalytic Properties of $TiO_2/NiO/Cu_2O$ Thin Films Prepared by Reactive Magnetron Sputtering, ***Toshiya Souma***, *I. Takano*, Kogakuin University, Japan

In recent years, various characteristics of TiO_2 have attracted considerable attention. One of their characteristics is a photocatalytic effect. The photocatalytic effect of TiO_2 shows antifouling or antimicrobial activity, and has the ability to decompose environmental pollutants. Thus TiO_2 has superior characteristics in many metal oxides, because its photo-excited state is very stable and does not cause self-decomposition. Therefore, TiO_2 can perform the electrolysis of water by light, however, a light reaction region of TiO_2 is limited within the ultraviolet region corresponded with only about 3 % of sunlight.

In this study, to improve the photocatalytic property of TiO_2 the $TiO_2/NiO/Cu_2O$ thin films were fabricated by laminating the TiO_2 layer with 3.0 - 3.2 eV and the Cu_2O layer with 2.2 eV in a band gap energy. In order to prevent the diffusion of Cu, the NiO layer was inserted between the TiO_2 layer and the Cu_2O layer. NiO has a high melting point, high hardness and has been used as a barrier layer. These three layers were prepared by reactive magnetron sputtering.

The film composition and microstructure were investigated by X-ray photoelectron spectroscopy and X-ray diffraction, respectively. Chromatic changes of a methylene blue solution were applied to the measurement of a photocatalytic property. Light irradiation to the $TiO_2/NiO/Cu_2O$ thin films in a methylene blue solution was carried out using a commercial sterilizing lamp as ultraviolet light and an artificial sun lamp as visible light. Transmittance of a methylene blue solution was measured by a spectrophotometer.

On the XRD measurement for the crystal structure of $TiO_2/NiO/Cu_2O$ thin films, the strong peaks of the anatase-rutile mixture from TiO_2 of the upper layer and the weak peaks of Cu_2O or NiO from the lower layer appeared. It was estimated that the diffusion of Cu from the Cu_2O layer was prevented by inserting the NiO layer. The suitable photocatalytic effect was obtained by inserting the NiO layer of 20 nm in a thickness and then the decomposition activity of a methylene blue solution showed about 57 % under an artificial sun light and about 77 % under a sterilization light. In the case of $TiO_2/NiO/Cu_2O$ thin films, it was considered that the role of the NiO layer was not only the protection of the diffusion but also the electric effect as a p-type semiconductor.

Vacuum Technology
Room: Hall 3 - Session VT-TuP

Vacuum Technology Poster Session

VT-TuP1 Estimating Measurement Uncertainty of Pressure Calibration, ***Yu-Wei LIN***, *C.-P. Lin, C.N. Hsiao*, National Applied Research Laboratories, Taiwan, Republic of China

A vacuum gauges calibration system for wide-range pressure was developed, and the measurement uncertainty associated with the system. The design of the system took into consideration of influencing factors that include uniformity of gas distribution and the geometric location of the gauge to be calibrated. The system operates following the procedure stipulated in the comparison vacuum gauge calibration method. The calibration may range from 10^5 to 10^{-5} Pa . The system makes use of capacitor vacuum gauge, SRG and hot cathode thermion vacuum gauge to estimate the degree of uncertainty associated with the system. The data collected from the gauge calibration tests indicated that if the background pressure of the system had reached 10^{-7} Pa, the uncertainty associated with the system were as follows: less than 3.6 % in the pressure range of 10^{-5} to 10^{-2} Pa, less than 2.3 % in the pressure range of 10^{-2} to 10^5 Pa. The present research has demonstrated the high stability of the vacuum calibration system, and its capabilities of conducting calibration for vacuum gauge with great efficacy.

VT-TuP5 The ESS Vacuum Control System Concept, ***Hilko Spoelstra***, *M. Zaera-Sanz*, European Spallation Source, Sweden

The European Spallation Source (ESS) is a high current proton LINAC to be built in Lund, Sweden. The LINAC will deliver 5 MW of power to the target at 2000 MeV, with a nominal current of 74 Ma. Ground break took place in September 2014 and the construction of the accelerator tunnel and adjacent buildings progresses rapidly.

Although the different LINAC sections will be in-kind contributions from the several member countries, the accelerator vacuum control system and the machine protection system, will be mainly designed and build in-house which requires a tight collaboration between the Integrated Control System Division (ICS) and the Vacuum Team of the Accelerator Division (AD) of ESS.

The Vacuum control system is based on PLC (Programmable Logic Controller) technology and on EPICS (Experimental Physics and Industrial Control System) SCADA (Supervisory Control and Data Acquisition). Each accelerator section has one or more PLCs to control the different valves by acting on the analog and interlock signals from the gauge- and pump-controllers through a pre defined voting scheme. EPICS modules will be used as the interface between the operator screen and the vacuum controllers. Besides local interlocks for vacuum, machine protection interlocks shall be integrated in the control system for the protection of the LINAC. This integration will provide beam permission to the beam interlock system when all nominal conditions for vacuum are met.

A set of control and machine protection functions will define the vacuum controls system architecture and implementation. This contribution will discuss the design of the ESS proton LINAC vacuum control system, strictly complying with all identified control and protection functions.

VT-TuP6 Effect of Impeller Tip Clearance on the Degree of Vacuum of Self-Priming Pump, ***Youn-Jea Kim****, H.J. Jeon, J.-H. Boo*, Sungkyunkwan University, Republic of Korea

Self-priming vacuum pump is hybrid-type pump of which the principles of axial-type screw vacuum pump and centrifugal pump are combined for better performance. It is operated by the rotation of inducer-impeller generating partial vacuum and centrifugal force. Due to its unique operating principle, self-priming vacuum pump is characterized for transferring fluid having viscosity and is able to be used in various industrial field treating multiphase fluids such as slurry. Tip clearance in self-priming vacuum pump is an important design factor affecting the performance of the pump, which is closely associated with the suction performance. In this study, the effect of impeller tip clearance on the degree of vacuum of self-priming pump was numerically investigated. Numerical analysis was conducted by ANSYS CFX ver. 16. The results for pressure and velocity distributions and H-Q curve were prepared with various values of tip clearance

VT-TuP7 Simulation of the Transporting of Sputtering Particles and Comparison of the Film Thickness Distributions between Simulations and Experiments, ***Kohei Kuroshima****, M. Iguchi,* Osaka Vacuum, Ltd., Japan*, S. Sugimoto*, Osaka Vacuum, Ltd.Osaka Vacuum, Ltd., Japan

A Monte-Carlo simulation of the transporting of sputtering particles was performed, using Born-Mayer potential as the two-body potential. Film thickness distribution on the substrate was calculated and compared to experimental results obtained under the same conditions. Calculations and experiments were made for a variety of gas pressures and target-substrate (T-S) distances.

The film thickness distribution on the substrate is determined by the distribution of particle emissions from the target, gas pressure and T-S distance. Therefore, if we can control the distribution of particle emissions, the pressure and the T-S distance, we can control the film thickness distribution on the substrate. The distribution of the transparent film thickness will create the designed Moire pattern.

Our simulations serve as basic research on this control.

VT-TuP8 Finite Element Based Multiphysics Analysis of Photon Stimulated Desorption from Vacuum Chamber used in Electron Storage Ring, ***Kamlesh Suthar****, B.K. Stillwell*, Argonne National Laboratory

We present preliminary study of the Photon Stimulated Desorption from aluminum vacuum chamber. Synchrotron radiation is generated in electron storage ring when the electron beam pass through magnetic field. In this paper, such synchrotron radiation is simulated on magnetic lattice of the storage beam. The temperature of the vacuum chamber increases due to absorption of photon beam simultaneously the molecular pressure also increases due to desorption of the adsorbed gases. This process of increasing in gases depends upon various physical phenomena, such as irradiation of photon beam due to interaction of electrons in applied magnetic field, secondary emission of electron from surface, heat transfer, and molecular flow of gases. Therefore, the solution of vacuum pressure inside the storage ring depends on various physics. This paper discusses preliminary results of analysis of vacuum pressure combining responsible physics.

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:

This work was supported in part by Office of Naval Research (USA) under Grant No. N00014-10-1-0181 and National Science Foundation (USA) under Grant No. DMR- 0855358.

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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 derived 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.

Actinides and Rare Earths Focus Topic
Room: 230A - Session AC+AS+MI-WeM

Magnetism, Complexity and Superconductivity in the Actinides and Rare Earths
Moderator: Tomasz Durakiewicz, Los Alamos National Laboratory

8:00am **AC+AS+MI-WeM1 The Valence-Fluctuating Ground-State of δ--Pu**, ***Marc Janoschek***, Los Alamos National Laboratory **INVITED**

Plutonium (Pu) is arguably the most complex elemental metal known because its 5f electrons are tenuously poised at the edge between localized and itinerant configurations. This complex electronic structure leads to emergent behavior—all a direct consequence of its 5*f* electrons—including six allotropic phases, large volumetric changes associated with these transitions of up to 25%, and mechanical properties ranging from brittle α-Pu to ductile δ-Pu. Pu also exhibits a Pauli-like magnetic susceptibility, electrical resistivity and a Sommerfeld coefficient of the specific heat that are an order of magnitude larger than in any other elemental metal. Finally, while experiments find no sign for static magnetism in Pu, most theories that use the correct volume predict a magnetically ordered state. This discrepancy might be reconciled by recent Dynamical Mean Field Theory (DMFT) calculations that suggest that the electronic ground state of δ-Pu is a quantum-mechanical admixture of localized and itinerant valence configurations. The question whether the ground state of δ-Pu is indeed a true quantum-mechanical superposition may only be answered via observation of the associated virtual valence (charge) fluctuations among the distinct 5f^4, 5f^5, and 5f^6 configurations. The characteristic energy scale for the associated spin fluctuations is expected to T_K= 800 K (E_{sf}≈ 70 meV) that will result in a dynamical spectral response centered at this energy for T < T_K. We have performed high-energy inelastic neutron spectroscopy at room temperature using a large polycrystalline sample of δ-^{242}Pu with a total mass of m ≈ 21 g at the Lujan Center and at the Spallation Neutron Source. Our measurements demonstrate the existence of high energy magnetic fluctuations centered at E_{sf} = 84 meV, in good agreement with the DMFT calculations. In addition, they allow us to extract the magnetic form factor of δ-Pu, yielding critical information about its valence state. These unprecedented results place show that the magnetism in Pu is not "missing" but dynamic, but dynamic, and is driven by virtual valence fluctuations. Our measurements provide a straightforward interpretation of the microscopic origin of the large, Pauli-like magnetic susceptibility of δ-Pu and associated Sommerfeld coefficient. Furthermore, because the various valence configurations imply distinct sizes of the Pu ion, the valence-fluctuating ground state of Pu also provides a natural explanation for its complex structural properties and in particular the large sensitivity of its volume to small changes in temperature, pressure or doping.

8:40am **AC+AS+MI-WeM3 Exchange Bias in Heterostructures Based on UO_2**, ***Evgeniya Tereshina***, Institute of Physics ASCR, Czech Republic*, Z. Bao,* PANalytical B.V., Netherlands*, L. Havela,* Charles University in Prague, Czech Republic*, R. Springell,* University of Bristol, UK*, S. Danis,* Charles University in Prague, Czech Republic*, A. Mackova,* Nuclear Physics Institute ASCR, Czech Republic*, T. Gouder, R. Caciuffo*, Institute for Transuranium Elements (ITU), Germany **INVITED**

Interfacial exchange interaction in bilayers consisting of two dissimilarly ordered magnetic materials (e.g. an antiferromagnet (AF) and a ferro- or ferrimagnet (F)) may give rise to a phenomenon called the magnetic exchange bias (EB) effect [1]. The EB manifests itself as a shift of a magnetic hysteresis loop along the field direction when the bilayer is field-cooled below the Néel temperature (T_N) of the AF. This property is of great value for magnetic recording applications. Despite the conceptual simplicity, a generally accepted theory that predicts the EB behavior for an apt pair of materials is still missing. The reason for that might be in poorly defined interface structure in both magnetic and crystallographic aspects.

Critical dependence of EB on magnetic anisotropy brings us the possibility to use actinides with strong spin-orbit interaction as the key ingredient. Here we report exchange bias studies in magnetic bilayers consisting of a stoichiometric UO_2 film grown epitaxially on different substrates and covered with polycrystalline metallic ($Ni_{80}Fe_{20}$ and Fe) and highly textured oxide (Fe_3O_4) layers of variable thickness. Large longitudinal exchange bias ~2.6 kOe is found in UO_2/Fe_3O_4 bilayers [3] while UO_2 combined with metallic ferromagnets displays perpendicular exchange coupling with an order of magnitude smaller EB. Interestingly, unusual effects in UO_2/Fe_3O_4 were observed, namely, exchange bias did not vanish at T_N of UO_2. Apart from the fact that single layers of magnetite were showing some EB (not more than 25 % of the total effect in UO_2/Fe_3O_4), the EB in UO_2/Fe_3O_4 bilayers exceeded notably that of the single Fe_3O_4's to approx. 70 K that was attributed to possible proximity effects of Fe_3O_4 on T_N of UO_2 and/or to the magnetic anisotropy of UO_2 preserved locally above T_N. The effects were observed for the samples of quality controlled by different methods such as X-ray Photoelectron Spectroscopy, conventional X-ray Diffraction, Transmission Electron Microscopy and Rutherford Backscattering Spectroscopy. The work has been supported by the Czech Science Foundation, grant No. 13-25866P.

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9:20am **AC+AS+MI-WeM5 Transport and Magnetism of 4f and 5f Systems: What we can Learn from Thermoelectric Power**

Krzysztof Gofryk, Idaho National Laboratory **INVITED**

The interplay between different electronic ground states, especially magnetism and superconductivity, has evolved in a climate of discovery in which many of the fundamental rules of condensed matter physics are questioned by materials with unexpected properties. These "emergent properties," such as complex magnetism, heavy-fermion superconductivity, the coexistence of magnetism and superconductivity, and/or Kondo physics emerge from complex materials in which quasiparticles develop different states of organization and correlation. The majorities of these bizarre electronic ground states are encountered in *f*-electron systems and are linked to the hybridization between the *f*-states and ligand electrons. How these properties evolve with the progressive filling of the *f*-shells remains an open question, but it is a key ingredient for their understanding. The 4*f* and 5*f* strongly correlated electron systems at the border of magnetism are of active current interest, particularly because the accompanying quantum criticality provides a route towards both strange-metal, non-Fermi-liquid behavior, and unconventional superconductivity. In spite of large theoretical and experimental efforts the nature of the electronic behaviors is still unclear. One way to address the electronic properties of these fascinating materials is it to perform extensive transport studies such as Hall, Nernst, or Seebeck effects. In particular, the latter one has gained importance in recent years in thermoelectric materials as potential solutions for applications, such as spot cooling of electronic components, waste heat recovery system and/or remote power generation in space stations and satellites. In addition, the Seebeck coefficient is a sensitive probe of energy relative to the Fermi level, it can therefore be used as a tool to characterize the electronic structure of materials, especially in the vicinity of the narrow gap or pseudo-gap. During the talk I will provide a general introduction to the magnetic and transport characteristics of 4*f* and 5*f* electron systems. Then, I will present thermoelectric properties of selected 4*f* and 5*f* materials and give an overview on how the thermoelectric power studies can be used to probe electronic properties in this class of materials. I will discuss implications of the results, and their limitations.

11:00am **AC+AS+MI-WeM10 Magnetic Properties of 2-2-1 Rare-earth and Uranium Compounds and their Interaction with Hydrogen**

Silvie Maskova, Charles University, Prague, Czech Republic, *R.V. Denys,* Institute for Energy Technology, Kjeller, Norway, *I. Halevy,* Nuclear Research Center Negev, Beer-Sheva, Israel, *K. Miliyanchuk, L. Akselrud,* Ivan Franko National University of Lviv, Lviv, Ukraine, *A. Kolomiets,* Lviv Polytechnic National University, Lviv, Ukraine, *V. Yartys,* Institute for Energy Technology, Kjeller, Norway, *M. Giovannini,* University of Genova, Genova, Italy, *L. Havela*, Charles University, Czech Republic

We have been studying some members of large family of A_2T_2X (A = Rare-Earth (RE) or actinide, T = transition metal, X = *p*-metal) compounds crystallizing in the Mo_2FeB_2 structure type (space group *P*4/*mbm*). U_2T_2X interact with H_2 only at high pressure (≈ 100 bar) reaching 2 H/f.u. The H absorption produces a lattice expansion, while the tetragonal structure is preserved. The H atoms presumably enter the 8*k* position inside the U_3T tetrahedra occupied randomly up to 50%. On the other hand, it was found that some RE_2T_2X compounds can absorb more hydrogen compared to their U-counterparts in much lower H pressures. The amorphization of the structure upon hydrogenation (4 H/f.u.) was found for $RE_2Pd_2In(Sn)$ with light RE (La, Nd). $RE_2Pd_2In(Sn)$ with heavy RE behave similar way as U_2T_2X compounds (2 H/f.u., crystal structure type not changed). For the isostructural indide Nd_2Ni_2In the hydrogen absorption of 7 H/f.u. leads to the orthorhombic distortion of the crystal structure.

Recently, we have been studying several isostructural RE_2T_2Mg (T = Ni, Pd). The H absorption in these compounds depends on the type of transition metal. The compounds with Ni tend to absorb up to 8 H/f.u. The crystal structure is changed to monoclinic (space group *P*21/*c*). If the transition metal is Pd, the hydrogen absorption is lower, reaching approx. 6 H/f.u. and the crystal structure is modified in different way. The Tb_2Pd_2Mg-hydride crystallizes in a new ternary structure type (*Fmmm*). In the case of Mg-compounds, the hydrogen absorption in not reversible. Upon desorption of H the initial crystal structure is not restored.

We have found that in U-compounds the ordering temperatures increase upon hydrogenation contrary to the RE-compounds where the ordering temperatures are dramatically reduced. Magnetic properties of U-compounds strongly depend on the inter-U distances. Hydrogen intrusion modifies the lattice by expanding it without changing the crystal-structure type leading to a band narrowing. As a consequence doping of U intermetallics by interstitial hydrogen leads to stronger magnetic properties. On the other hand, the hydrogen absorption has opposite effect on magnetic properties of RE_2T_2X compounds. For RE compounds, hydrogenation affects mainly the 4*f* – magnetic moments and their ordering. The exchange coupling is reduced presumably by reducing the concentration of conduction electrons.

11:20am **AC+AS+MI-WeM11 Structural, Electronic, and Magnetic Characteristics of Np_2Co_{17} and Analogue Compounds Under Pressure**

Itzhak Halevy, Nuclear Research Center Negev, Israel, *A. Hen,* Institute for Transuranium Elements (ITU), Germany, *I. Orion,* Ben Gurion University, Israel, *E. Colineau, R. Eloirdi, J.C. Griveau,* ITU, Germany, *F. Wilhelm, A. Rogalev,* ESRF, France, *N. Magnani, A.B. Shick, R. Caciuffo*, ITU, Germany

A previously unknown neptunium-transition-metal binary compound Np_2Co_{17} has been synthesized and

characterized by means of powder x-ray diffraction, ^{237}Np Mössbauer spectroscopy, superconducting-quantum-interference-device magnetometry, and x-ray magnetic circular dichroism. The compound crystallizes

in a Th_2Ni_{17}-type hexagonal structure with room-temperature lattice parameters a= 8.3107Å and c=

8.1058Å. Magnetization curves indicate the occurrence of ferromagnetic order below T_C>350 K. Mössbauer

spectra suggest a Np^{3+} oxidation state and give an ordered moment of $\mu_{Np}=1.57\mu_B$and μNp=$1.63\mu_B$

for the Np atoms located, respectively, at the 2*b* and 2*d* crystallographic positions of the $P6_3/mmc$ space group.

Combining these values with a sum-rule analysis of the XMCD spectra measured at the neptunium *M*4,5 absorption

edges, one obtains the spin and orbital contributions to the site-averaged Np moment [$\mu_S=-1.88\mu_B$,

$\mu_L=3.48\mu_B$]. The ratio between the expectation value of the magnetic-dipole moment and the spin magnetic

moment ($m_{md}/\mu_S=1.36$) is positive as predicted for localized 5*f* electrons and lies between the values

calculated in intermediate-coupling (IC) and *jj* approximations. The expectation value of the angular part of

the spin-orbit-interaction operator is in excellent agreement with the IC estimate. The ordered moment averaged

over the four inequivalent Co sites, as obtained from the saturation value of the magnetization, is μ_{Co}~$1.6_{\mu B}$.

The experimental results are discussed against the predictions of first-principles electronic-structure calculations

based on the spin-polarized local-spin-density approximation plus the Hubbard interaction. The structural behavior of Np_2Co_{17} is investigated by means of high pressure diamond-anvil compression measurements and is compared with that of the isostructural compounds Lu_2Co_{17} and Lu_2Ni_{17}. The Th_2Ni_{17}-type hexagonal crystal structure is preserved with no measurable discontinuous volume collapses up to the highest achieved pressure, p=43GPa. For Np_2Co_{17}, fits to the Birch-Murnaghan and Vinet equations of state give values of the isothermal bulk modulus and

its pressure derivative of B_0=286GPa and B_0=3, revealing that this Np compound is a highly incompressible solid with stiffness comparable to that of superhard covalently bonded materials. The isothermal equation of state for the studied compounds are in excellent agreement with the results of *ab initio* fully-relativistic, full potential local spin-density functional calculations. Theoretical estimates of the bulk modulus are given also for Np_2Ni_{17}, for which B_0 is predicted to assume values intermediate between those measured for Lu_2Ni_{17} and Np_2Co_{17}.

11:40am **AC+AS+MI-WeM12 Alloying UH_3 as a Probe into the 5*f* Magnetism**

Ladislav Havela, *M. Paukov, I. Tkach, M. Cieslar, Z. Matej, D. Kriegner, D. Drozdenko, I. Turek, M. Divis,* Charles University, Czech Republic, *N.-T.H. Kim-Ngan*, Pegagogical University, Poland

Several routes of preparation of alloyed U trihydrides, UH_3, were discovered. Starting from the U_6T compounds, hydrogenation leads to T atoms embedded in the β-UH_3 structure, with transition-metal atoms T occupying one of the U sites. We have been hydrogenating γ-U alloys, using various transition metals helping (together with ultrafast cooling) to retain the bcc U structure down to low temperatures. As such alloys are much more resistant to hydrogen attack, high pressures of H_2 gas had to be applied. The H absorption corresponds to approx. 3H/atoms per 1 U atom. In none of the cases the alloying metals segregate and two different structures were obtained. The hydrides $(UH_3)_{1-x}Zr_x$ form the α-UH_3 structure, i.e. the bcc structure expands and fills by H. Hence basic electronic properties of α-UH_3 could be established. Starting from $U_{1-x}Mo_x$, we obtained $(UH_3)_{1-x}Mo_x$, which tends to be β-UH_3 like, but has the grain size is 1 nm only, i.e. practically amorphous. This amorphous phase also easily accepts additional dopants, as Zr, Fe, Ti, V...however magnetic properties remain only weakly affected. It is quite remarkable that all such materials are ferromagnets with the Curie temperature in the range 160-205 K, even if the active U sublattice is diluted by more than 30% of other metals. In this respect the hydrides are different than conventional band ferromagnets, sensitive to inter-atomic spacings and alloying. Albeit all are metallic, the U-H interaction, which can have a partly ionic character, plays clearly important role. Electronic structure calculations (performed for the α-UH_3 structure and in ferromagnetic or Disordered Local Moment state, with possible random Zr occupancy) suggest a transfer of U-6d and 7s electrons into H-1s states, reducing the hybridization of 5f and non-f states, supporting thus magnetism even if the U-U spacing is below the Hill limit [1].

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Additive Manufacturing/3D Printing Focus Topic
Room: 211B - Session AM+EM+MS+TF-WeM

Materials, Designs, and Applications of Additive Manufacturing
Moderator: Erik B. Svedberg, The National Academies

8:00am **AM+EM+MS+TF-WeM1 An Overview of Additive Manufacturing**, ***Ed Morris***, *R. Gorham*, NCDMM **INVITED**

“An Overview of Additive Manufacturing” - Additive manufacturing, also called 3D printing, has captured worldwide attention. Many believe that it is introducing the next industrial revolution because of its impact on product innovation and its unique manufacturing capabilities. America Makes – National Additive Manufacturing Innovation Institute is the first Manufacturing Innovation Institute established as part of a National Network for Manufacturing Innovation. Mr. Ed Morris, Director of America Makes and Vice President, National Center for Defense Manufacturing and Machining, will give an overview of additive manufacturing, and will discuss America Makes’ actions to accelerate the use of additive manufacturing technologies in the United States and increase our nation’s global manufacturing competitiveness.

8:40am **AM+EM+MS+TF-WeM3 Material Considerations and Opportunities for Laser Powder Bed Additive Manufacturing**, ***Michael W. Peretti***, *D.H. Abbott*, General Electric Aviation **INVITED**

Additive Manufacturing (AM) has the potential to be a significant supply chain disruptor over traditional means for manufacturing a broad range of components for aerospace and other demanding applications. The ability to unlock complex, high-performance designs while reducing part count and number of manufacturing steps is beginning to revolutionize the way we think about making things. One of the key areas of development to further expansion of opportunities for AM is the production and supply of high-quality raw materials. This presentation discusses the critical issues for AM input raw materials, with particular emphasis on metal powder input stock for laser powder bed AM processes. Some background and experience from GE Aviation’s development of the LEAP fuel nozzle will be shared, along with comments on the direction that the AM industry could take and the role of and potential for AM-specific metal powder alloys.

9:20am **AM+EM+MS+TF-WeM5 High Quality and High Speed EBM 3D Printing by the Integration of High Performance Electron Sources**, ***Colin Ribton***, TWI Ltd., UK, *S. del Pozo*, TWI Ltd. and Brunel University, UK

Production of high integrity components must use smart manufacturing methods to be efficient in use of scarce materials and other resources, and must ensure its environmental impact is minimized. Advanced manufacturing techniques, such as metal powder bed 3D printing , can be carried out by selective laser melting (SLM) or electron beam melting (EBM). In both cases the component is built layer by layer, with a beam as an intense energy source drawing each layer by melting powder. EBM is significantly faster than SLM and has been used to create metal parts in large quantities over the past 5 years. EBM machines have produced many tens of thousands of orthopedic implants. There are a number of key benefits in employing this manufacturing technology – including ‘complexity for free’, efficient use of material and flexibility of design. Increasingly, the aerospace industry is investigating the use of EBM for the manufacture of aircraft components and aero engine parts. However, the size of many of these components presents challenges to the EBM process in production rate and quality consistency over long build times (i.e. 150 hours).

The aim of this work is to overcome key obstacles concerning future requirements for EBM 3D printing for production of aerospace parts through the integration of two enabling technologies. The work will develop and integrate a novel plasma cathode electron source with an EBM machine focusing on realizing the enhanced capabilities of low maintenance, consistent manufacturing performance and higher productivity. Also, development and integration of an array probe device will provide quantified quality assurance of machine manufacturing readiness. The key research challenges will be the design of the electron source and optics and the development of new build procedures making best use of the new source.

The equipment will enable the wider adoption of EBM leading to efficient use of materials – particularly strategic titanium alloys and nickel based super alloys at first.

9:40am **AM+EM+MS+TF-WeM6 Laser Induced Forward Transfer of High-Viscosity, Polymer-Based VO_2 Inks**, ***Eric Breckenfeld***, *H. Kim, T. Sutto, N. Charipar, A. Piqué*, Naval Research Laboratory

Additive manufacturing direct-write processes such as direct-write assembly, micropen, inkjet, and laser-induced forward transfer (LIFT) have become increasingly popular as interest in printable electronics and maskless patterning has grown. Compared to conventional lithography, these additive manufacturing processes are inexpensive, environmentally friendly, and well suited for rapid prototyping and large-area applications. At the same time, researchers have pursued various chemical solution deposition processes for combining additive manufacturing technology with functional electronic materials. Among a multitude of transition-metal oxides, vanadium dioxide (VO_2) has emerged as a material of particular interest due to its sharp semiconductor-to-metal phase transition near room temperature. A set of distinct optical and electronic properties which arise as a result of this transition have made VO_2 popular for thermochromic coatings, resistive switching, optical storage, light modulators, and other applications. Here, we demonstrate the development of a polymer-based solution for the deposition of VO_2 thin films. By exploring a variety of sintering and annealing conditions as well as exploring different polar solvents, we have optimized the growth of these films on glass and crystalline substrates. We go on to explore printing of VO_2 devices via the LIFT technique, which is notable for its ability to print high-viscosity inks and pastes. Finally, we will discuss our efforts toward the development of low temperature laser sintering in order to realize VO_2 films on substrates incompatible with high furnace temperatures.

11:40am **AM+EM+MS+TF-WeM12 Printing Multi-Functionality using Additive Manufacturing**, ***Ryan Wicker***, University of Texas at El Paso **INVITED**

Since the commercial introduction of Additive Manufacturing (AM) technologies more than two decades ago, considerable advancements in processing speed, accuracy, resolution and capacity have been achieved and the available AM materials have expanded considerably, enabling customized end-use products to be directly manufactured for a wide range of applications. Many AM technologies have been released that use different processes for fabricating the individual layers from a variety of liquid, solid, and powder-based materials ranging from photoreactive polymers to metals. In 2000, the University of Texas at El Paso identified AM as an emerging technology and invested strategically in establishing the W.M. Keck Center for 3D Innovation (Keck Center). The Keck Center has grown to occupy over 13,000 sq. feet with more than 50 commercial and experimental AM machines, representing 10 system manufacturers, nine distinct layer processing methods, and several custom AM-based patented and patent-pending systems. One particular focus of Keck Center research is on developing the methods and systems required to have automated control over material placement and structure creation, leading to, for example, the realization of complex 3D devices that integrate electronics and thus intelligence within mechanical structures as well as 3D spatially complex bioactive, implantable, tissue engineered constructs. There are myriad issues associated with combining multiple materials to create functional products – from the deposition and processing of different materials to the combined performance of the materials in the resulting product. Despite these issues, the opportunities for AM in aerospace, defense, biomedical, energy and enumerable other applications continue to expand as the achievable length scales in AM decrease, the number of materials available for use in AM increases, the performance of these materials are characterized and controlled in the final product, and new strategies for integrating AM with other manufacturing technologies are successfully demonstrated.

Applied Surface Science
Room: 212D - Session AS-WeM

Practical Surface Analysis II: Influence of Sample Preparation and Novel Sample Prep Techniques
Moderator: Gregory Herman, Oregon State University, Kathryn Lloyd, DuPont Corporate Center for Analytical Sciences

8:00am **AS-WeM1 ASSD 30th Anniversary Lecture: A Historical Perspective of the Materials Challenges and Instrumentation Solutions Available for Practical X-ray Photoelectron and Auger Electron Spectroscopy**, ***John Moulder***, Physical Electronics USA **INVITED**

During the first 30 years of the Applied Surface Science Division's (ASSD) existence the changing world around us has driven the need for new materials for a wide range of applications including: higher performance coatings, structural materials, electronics, data storage devices, display and printing technology, energy storage devices, and many more. For most of these materials systems the composition of a surface, interface, thin film or nanostructure plays a critical role in the performance of the material. During the same period of time, analysts have endeavored to characterize these new materials and instrument manufacturers have endeavored to provide the analytical capabilities required by the analyst to answer critical questions about the materials being studied.

When the ASSD was formed in the 1985 the second generation of XPS and AES based surface analysis instrumentation was emerging and surface analysts were characterizing structural materials, catalysts, thin film coatings, semiconductor devices, magnetic storage media, and more. Common challenges faced by the analyst included quantification, insulator analysis, micro area analysis, the desire for more chemical information, the desire for 2D and 3D information, and keeping up with the demand for more data.

This presentation will provide a historical perspective on the evolution of both the materials challenges faced by surface analysts and the XPS and AES instrumentation that became commercially available to address these challenges. Finally we will comment on where we are today and possible future directions.

8:40am **AS-WeM3 Using Argon clusters for Improved XPS Information**, ***Jonathan Counsell***, *S.J. Coultas, C.J. Blomfield, D. Surman, C. Moffitt*, Kratos Analytical Limited, UK

A thin layer of carbonaceous material is commonly found on the surface of air exposed samples - this layer is generally known as adventitious carbon. Adventitious carbon is generally comprised of a variety of relatively short chain, perhaps polymeric hydrocarbons species with small amounts of both singly and doubly bound oxygen functionality. Even brief exposures to atmosphere will produce a thin overlayer. During XPS analysis this overlayer has the unfortunate effect of attenuating the signal from the material underneath decreasing the signal strength and intensity. Furthermore, the presence of Carbon and Oxygen also add complexity to the peak fitting and assignment of high resolution spectra of these elements. For analysts it is seen as a hindrance when wanting to know the "real" surface chemistry

In recent times Argon cluster ions have been used to depth profile soft materials. The cluster ion sputters away sample material however the collision mechanism limits the propagation of damage into the sample bulk. This new method has been widely exploited with polymeric thin-films and biomaterials[1]. Here we will discuss the use of Argon cluster ions as a novel way to remove adventitious carbon to improve the information obtainable through analysis. Improvements in both sensitivity and detection limit will be discussed as well as improved spectral resolution. We will also demonstrate how Argon cluster cleaning can improve the spatial resolution of XP imaging. A variety of systems will be discussed to demonstrate the broadness of the application. A comparison with low energy monatomic Argon cleaning is also made including discussion ion incorporation and lattice damage.

[1] P. Cumpson, J. F. Portoles, N. Sano, and A. J. Barlow, *J. Vac. Sci. Technol. B* 31(2), 2013.

9:00am **AS-WeM4 *In Situ* Chemical Imaging of Environmental Liquid Surfaces and Interfaces Using Microfluidics and Dynamic ToF-SIMS: Toward Multimodal and Mesoscale Imaging**, ***Xiao-Ying Yu***, *Z. Zhu*, Pacific Northwest National Laboratory

The surfaces of aqueous phases and films have unique kinetics and thermodynamics, distinct from the bulk. However, major surface analytical techniques are mostly vacuum-based and direct applications for volatile liquid studies are difficult. We developed a vacuum compatible microfluidic interface, System for Analysis at the Liquid Vacuum Interface (SALVI), to enable direct observations of liquid surfaces and liquid-solid interactions using time-of-flight secondary ion mass spectrometry (ToF-SIMS). The unique aspects of this R&D 100 award winner include the following: 1) the detection window is an aperture of 2-3 mm in diameter allowing direct imaging of the liquid surface, 2) surface tension is used to hold the liquid within the aperture, and 3) SALVI is portable among multiple analytical platforms. SALVI is composed of a silicon nitride (SiN) membrane as the detection area and a microchannel made of polydimethylsiloxane (PDMS). Its applications ToF-SIMS as an analytical tool were evaluated using a variety of aqueous solutions and complex liquid mixtures, some of which contain nanoparticles. SALVI was also used to investigate the solvent structure of switchable ionic liquids. Recently, we demonstrated *in situ* probing of the electrode-electrolyte solution interface (or solid-electrolyte interface, SEI) using a new electrochemical SALVI. It provides the first direct observation of the surface and diffused layer of SEI in a liquid with chemical speciation using dynamic ToF-SIMS. Moreover, SALVI was extended for studying biofilm growth and single mammalian cells using correlative imaging by more than one spectroscopy and microscopy technique, each offering different spatial and temporal scales. That is, collecting data on different information level from an identical area in the same sample ideally could lead to a more holistic view of the hierarchical structural organization of complex systems in the real world. Selected results from our latest development will be presented, showcasing new directions and applications of multimodal imaging of environmental surfaces and interfaces and studying chemistry from the bottom up, all based on microfluidics. SALVI, a portable microfluidic reactor, sets the analytical foundation toward chemical imaging of complex phenomena occurring in multiple time and length scales, or the mesoscale, underpinning chemical changes at the molecular level.

9:20am **AS-WeM5 A VAMAS Inter-laboratory Study of the Measurement of Chemistry and Thickness of Nanoparticle Coatings**, ***David Cant***, *N.A. Belsey, C. Minelli, A. Shard*, National Physical Laboratory, UK

Nanoparticles with a coating or shell are widely studied in both academic and industrial research. X-ray Photoelectron Spectroscopy (XPS) and Low/Medium Energy Ion Scattering (LEIS/MEIS) have potential for accurate measurement of chemistry and thickness of nanoparticle coatings, but the accuracy of these measurements is dependent upon correct modelling for analysis and reproducibility of sample preparation. There is as yet no uniform approach to these issues; to address this, VAMAS project A19 – an interlaboratory study involving 24 participants in 12 countries – has been undertaken with the following objectives:

- Assessment of inter-laboratory variability in measuring nanoparticle coating thickness
- Comparison of sample preparation techniques.
- Testing variability of procedures for quantitative analysis.

Samples were prepared from commercial gold colloid and incubated with a short peptide. Each participant received one pre-deposited sample on Si wafer, and one solution (and Si wafer) for their own in-house deposition. Participants were requested to return their samples to help identify the effect of differences in sample deposition between pre-deposited and in-house samples.

Thickness values reported by participants performing XPS were compared to values calculated from reported atomic concentrations using the *T*(NP) method [1,2]. A significant difference was observed between thicknesses determined for the pre-prepared sample and those determined for samples deposited by the participants in-house. Thicknesses determined for the in-house samples were larger than those determined for the pre-deposited samples. This was attributed to increased hydrocarbon presence observed in the C 1s spectra – likely caused by uneven sample deposition allowing detection of substrate contamination. In some cases, both pre-deposited and in-house samples exhibited abnormally low calculated thicknesses, potentially due to damaging of the coating by the x-ray beam.

The results of this study will assist in the development of a new ISO standard on the measurement of surface chemistry and thickness of nanoparticle coatings. The study will also provide information relevant to the ISO standard for reporting information related to the history, preparation, handling and mounting of nanomaterials prior to analysis, currently in development under ISO TC201. The production of guidelines for the measurement of nanoparticle coatings and sample preparation will be of great use in commercial applications of coated nanoparticles.

References

[1] Shard, A.G., Journal of Physical Chemistry C, 2012. 116(31): 16806-16813

[2] Belsey, N. A., Shard, A. G., Minelli, C. Biointerphases, 2015. 10, 019012

11:00am **AS-WeM10 A Quantitative Quest: Single Cell Analysis by LG-SIMS**, ***Christopher Szakal***, National Institute of Standards and Technology (NIST)

Large geometry secondary ion mass spectrometry (LG-SIMS) has been used extensively for particle analyses and geochemical analyses, owing to its ability to maintain adequate mass resolution while operating at high secondary ion transmission. Efforts will be presented that extend the knowledge acquired in these application areas to single cell analyses of elemental species. To be useful, LG-SIMS results likely need to be quantitative for the amounts of a given element per cell and/or in ratios of different elements within each cell. Approaching this level of detail requires the establishment of the natural variability of such data from cell-to-cell, the reproducibility of the measurement technique, and whether the data is relevant to pertinent questions about the cellular population. Progress will be shown towards achieving these aims for single bacterial cells, including sample preparation necessary for such measurements, technique-specific considerations, and analytical figures of merit for LG-SIMS elemental ratios. Prospective application areas will be presented, along with potential pitfalls of such an approach.

11:20am **AS-WeM11 Ambient Mass Spectrometry Imaging of Live Cells and Tissues**, *J.K. Kim,* ***DaeWon Moon***, DGIST, Republic of Korea

Currently, mass spectrometry imaging is based on Secondary Ion Mass Spectrometry (SIMS) and Matrix-Assisted Laser Desorption and Ionization (MALDI). Generally specimens for SIMS and MALDI are prepared by cryo-section and drying, which modifies the intrinsic biology due to sample preparations and subsequently does not allow dynamic response studies of biosystems to various chemical and physical stimuli. Most of recently developed ambient mass spectrometry have the spatial resolution in the range of ~50 µm, lacking in celluar and subcellular imaging of cells and tissues.

To investigate the intrinsic biology and dynamic responses of live cells and tissues in the cellular level, we developed an ambient imaging mass spectrometry system with ~5 µm spatial resolution. The ambient imaging mass spectrometry is based on low temperature plasma-surface reaction and desorption and ionization of surface products using near IR (808 nm) laser. Mass imaging is based on the movement of the sample stage. To enhance the laser desorption and ionization, Au nanorods of 10 nm diameter and 40 nm length were used. To further enhancement of sensitivy and possibly membrane specificity, liposome conjugated Au nanorods were used. An orbitrap mass spectrometer with a differential pumping and a pumping load adjustment is used as a mass analyzer.

Colonies of HCT-8 cells and hypothalamus tissues were mass imaged. Hypothalamus tissues were prepared with vibrotome, which allow sectioning of a hypothalamus tissue without freezing. Approximately 40 mass peaks from ~80 amu upto ~ 350 amu were observed with mass imaging. Single cells were observed clearly form a colony of HCT-8 cells and a hypothalamus tissue. Indentification of imaged mass peaks are in progress with mass reference data and mass-mass analysis.

11:40am **AS-WeM12 Intricacies of Sample Preparation for ToF-SIMS Analysis of Biological Specimens**, ***John Fletcher***, Chalmers University of Technology, Sweden **INVITED**

Biological and medical research is a popular and expanding area of application for time-of-flight secondary ion mass spectrometry (ToF-SIMS). The ability to perform such analyses has greatly benefited in recent years from the introduction of new ion beams that generate more signal from intact molecular ions that are generally more chemically characteristic and so aid in the interpretation of the complex spectra generated from biological specimen. The introduction of polyatomic ion beams such as C_{60} heralded the dawn 3D molecular imaging with ToF-SIMS and most recently gas cluster ion beams such as Ar_{4000} have shown dramatic improvements for the detection of intact lipid species from tissue.

However, such advances are meaningless if the information from the analysis is erroneous due to artefacts introduced during the preparation of chemically complex, and delicate, biological samples such as cells and tissue sections. Analysis of samples in a frozen hydrated state is often considered to be the best approach for maintaining the integrity of the sample but is not always possible or practical. In this presentation the implications of different preparation approaches are presented and discussed and methods for removing artefacts due to imperfect sample preparation are presented.

Biomaterial Interfaces
Room: 211D - Session BI-WeM

Biomolecules at Interfaces
Moderator: Axel Rosenhahn, Ruhr-University Bochum

8:00am **BI-WeM1 Understanding Hydration of Proteins by SALVI and Liquid ToF-SIMS**, ***Jiachao Yu****, Y. Zhou, X. Hua, Z. Zhu,* Pacific Northwest National Laboratory*, S. Liu,* Southeast University, China*, X.-Y. Yu*, Pacific Northwest National Laboratory

Hydration is crucial to the structure, conformation, and biological activity of proteins. Proteins without water molecules surrounding them would not have viable biological activity. Specifically, water molecules will interact with the surface and internal structure of proteins, and different hydration states of proteins make such interactions distinct. Thus, it is important to understand the hydration of proteins on surfaces, which can provide a fundamental understanding of the mechanism of their structure, conformation, and biological activity. Our group developed an important technique to study liquid surfaces and interfaces, namely System for Analysis at the Liquid Vacuum Interface (SALVI). It has been recently applied to study hydrated protein biofilms. SALVI is a vacuum compatible microfluidic device that consists of a SiN window as the detection area and a microchannel made of polydimethylsiloxane (PDMS). The protein solution was introduced into the microchannel. After incubating for a period of time, a hydrated protein biofilm formed on the back side of the SiN membrane. The information of hydrated proteins was collected using the time-of-flight secondary ion mass spectrometry (ToF-SIMS) in the SALVI device in the liquid state. Compared with previous results from dry protein samples, we not only confirmed the amino acid compositions of proteins, but also firstly discovered that the distribution of water molecules surrounding and inside proteins were varied among different types of proteins. Our liquid ToF-SIMS results show that 1). The water clusters number and relative counts vary among the same hydrated proteins, which imply that the distribution of water molecules surrounding and inside a protein is inhomogeneous; 2). The same water clusters have varied content in different types of proteins, which indicate that the distribution of water molecules have a strong relationship with the structure and conformation of the proteins at the biointerface. These first observations of hydrated protein biofilms on a surface will pave the investigation of the structure, conformation, and biological activity of proteins in the future.

8:20am **BI-WeM2 Direct Measurement of the Interaction Free Energies of Single Hydrophobic Peptides with Extended Hydrophobic Surfaces**, ***Philipp Stock****, T. Utzig, M. Valtiner*, Max-Planck Institut für Eisenforschung GmbH, Germany

Placing hydrophobes into an aqueous medium gives rise to what is well known as so-called hydrobobic interaction (HI) or hydrophobic force. This thermodynamic driven force gives rise to interaction and/or self-organisation of solvated hydrophobes in water. Famous examples are protein folding, lipid-bilayer membrane stability and enzymatic catalysis.

Here we will describe a SM-AFM setup to measure the interaction free energies (ΔG_0) of eight different hydrophobic peptides interacting with extended hydrophobic surfaces. First, we estimate the free energy of a single hydrophobic unit interacting with an extended hydrophobic surface. Secondly, we measured the change in free energy upon increasing the number of hydrophobic units in different sequences (synergies vs antagonistic effects).

In particular, we studied the change in free energy by placing a spacer groups (glycine) between the hydrophobic units. Interestingly our data shows that the interaction free energy scales with the number of hydrophobic units. Each hydrophobic unit seems to contribute about 4.8 kT. As such we observe a good agreement with values measured for two interacting benzene molecules in water.

Hence, hydrophobic interaction energies of hydrophobic surfaces with hydrophobic peptide fragments on a flexible peptide chain seem to linearly add up, irrespective of the incorporation sequences.

8:40am **BI-WeM3 Cells and Extracellular Matrices as Smart Materials: Dissecting and Rebuilding Mechaniobiological Units**, ***Sanjay Kumar***, University of California, Berkeley **INVITED**

Living cells are capable of processing a variety of mechanical signals encoded within their microenvironment, which can in turn act through the cellular structural machinery to regulate many fundamental behaviors. In this sense, cells may be regarded as "smart materials" that dynamically and locally modulate their physical properties in response to environmental stimuli. I will discuss our recent efforts to understand and control these living materials, and to create new, bio-inspired materials that mimic sequence/structure/function relationships of cytoskeletal networks. Key areas of emphasis will include: (1) Understanding and targeting biomechanical regulation of tumor infiltration in the brain; (2) Engineering stimulus-sensitive intrinsically disordered protein brushes based on neuronal cytoskeletal networks. These efforts exemplify the important notion that biomaterials can be extremely valuable platforms with which to understand and control cell behavior, and that understanding cellular structural networks can yield unexpected insights that inform the creation of novel biomaterials.

9:20am **BI-WeM5 Molecular Modeling of Biofunctionalized Hydrogels to Guide Hydrogel Design**, *X. Li,* Clemson University*, M.L. Becker,* University of Akron*, N.S. Murthy,* Rutgers University*, **Robert Latour***, Clemson University

Peptide-functionalized PEG-based hydrogels represent the workhorse material for tissue engineering and regenerative medicine applications because of their potential to mimic the extracellular matrix and serve as a substrate to direct cellular response. In order for a bioconjugated hydrogel to exhibit its intended bioactivity, the peptides that are tethered within the hydrogel must be accessible at the hydrogel surface for cell-receptor binding. Surface availability for a given peptide and hydrogel system will be a function of design parameters such as tether length, tether structure, and hydrogel crosslinking density. While the surface-accessibility of the peptide can be readily assessed experimentally, reasons for low accessibility (if encountered) are not easily determined. To address this type of problem, we are developing molecular modeling and simulation methods that will provide the ability to understand and visualize hydrogel behavior at an atomistic level to serve as a potentially powerful tool for hydrogel design. We are developing the molecular models using a multiscale approach. Coarse-grained (CG) parameters are first obtained from all-atom models of the various structural elements of the hydrogel system in aqueous solution using the polymer consistent force field (PCFF). A coarse-grained structure of the hydrogel is then first created at the experimental crosslink density using an efficient on-lattice method. The CG model is then removed from the lattice and equilibrated using the TIGER2 advanced sampling algorithm. The resulting equilibrated CG system is then reverse-mapped to an all-atom model. The all-atom model is then hydrated in water and equilibrated once more to yield the final predicted structure of the system. The resulting models are validated by comparing with structure-factor plots obtained by neutron scattering and/or X-ray diffraction. The resulting molecular models provide an atomistic-level view of peptide accessibility at the hydrogel surface. If low accessibility is encountered for a given design, the molecular models can provide clear direction regarding the cause of the problem and indicate the design changes that should be made to improve the bioactivity of the system.

9:40am **BI-WeM6 Physisorption of Stimuli-Responsive Polypeptides with Genetically Programmable Aqueous Phase Behavior**, ***Linying Li****, C. Mo, Q. Tu, N.J. Carroll, A. Chilkoti, S. Zauscher,* Duke University*, M. Rubinstein,* University of North Carolina at Chapel Hill*, G.P. López*, Duke University

The ability to control the physical adsorption (physisorption) of proteins to solid surfaces is of fundamental importance in the design of engineered bio-interfaces for many biomaterial, industrial and bioanalytical applications. We present a study of the kinetics of adsorption and consequent single- and multi-layered architectures of recombinant, intrinsically disordered proteins whose aqueous phase behavior is programmable at the sequence level. Elastin-like polypeptides (ELPs) are a class of engineered repetitive polypeptides that undergo a reversible, lower critical solution temperature (LCST) phase transition in water. Their phase behavior is programmable by tuning the amino acid sequence, concentration, and molecular weight of the ELPs. We used light scattering assays to investigate the phase diagrams of the peptides and quartz crystal microbalance with energy dissipation (QCM-D) to investigate the diffusion-limited adsorption kinetics of ELPs onto surfaces. Below the critical temperature, ELPs are soluble and only form single monolayers of peptides on surfaces upon adsorption, while above the critical temperature, ELPs phase separate, leading to multilayer adsorption. We used ellipsometry and atomic force microscopy (AFM) to characterize the thickness and roughness of the protein assemblies on surfaces. The elemental composition of the protein-modified surfaces was analyzed by X-ray photoelectron spectroscopy (XPS). Contact angle measurements were performed to examine the temperature-responsive nature of the surfaces. This study demonstrates that, based on their genetically encoded phase behaviors, the adsorption behavior of ELPs can be controlled to attain desired architecture, thermal-responsive behavior and functionality. It also provides insight into protein adsorption at the molecular level that can be useful in a number of contexts including immunoassays, drug delivery and cell culture.

11:00am **BI-WeM10 Evidence of a Molecular Boundary Lubricant at Snakeskin Surfaces**, ***Joe Baio****,* Oregon State University*, M. Spinner,* University of Kiel, Germany*, C. Jaye, D.A. Fischer,* National Institute of Standards and Technology (NIST)*, S. Gorb,* University of Kiel, Germany*, T. Weidner*, Max Planck Institute for Polymer Research, Germany

Snake scales have direct mechanical interaction with the environment. During slithering the ventral scales at a snake's belly are permanently in contact with the substrate, while the dorsal scales have an optical function for camouflage and thermoregulation. Recently it has been shown that ventral scales have adapted to this biological function and provide improved lubrication and wear protection compared with dorsal scales. While biomechanic adaption of snake motion to specific habitats is of growing interest in material science and robotics, the molecular level mechanism for the frictional influence of ventral scales is unknown. In this study, we characterize the outermost surface of snake scales using sum frequency generation (SFG) spectra and near edge x-ray absorption fine structure (NEXAFS) images collected from freshly molted California kingsnake (*Lampropeltis californiae*) scales. NEXAFS microscopy enables the mapping of specific molecular bonds at the C and N K-edges. The resulting NEXAFS images highlight the intensities of C=C π*, σ* (C−H), C=O π*, and amide π* bonds, demonstrating that the chemistry across the scale surfaces is uniform. SFG spectra at the amide I vibrational band (1550-1850 cm^{-1}) were collected from ventral and dorsal scales across three different individuals. Within the spectra taken from both types of scales, we observe a single peak at 1746 cm^{-1} that originates from ordered ester groups. In the CH stretching region, we observe two distinct vibrational modes in the spectra collected from the dorsal scale - 2850 and 2865 cm^{-1}. Both of these modes stem from symmetric CH_2 vibrations. Three bands are present in the CH spectra from the ventral scale - 2850, 2875, and a broad peak at 2975 cm^{-1}. Again, the peak at 2850 cm^{-1} is related to CH_2 symmetric vibrations, while the peaks at 2875 and 2975 cm^{-1} are related to symmetric and in plane anti-symmetric CH_3 stretches, respectively. Combined this analysis reveals the existence of a previously unknown lipid coating on the surfaces of both the ventral and dorsal scales with molecular structure closely related to their biological function: lipids on ventral scales form a highly ordered layer which provides both lubrication and wear protection at the snake's ventral surface.

11:20am **BI-WeM11 Selective Self-Assembly of Acidic Nanofibrils by a Calcite-Binding Barnacle Cement Protein**, *C. So,* National Research Council postdoc cited at Naval Research Laboratory*, J. Liu, K. Fears, D. Leary, J. Golden, **Kathryn Wahl***, US Naval Research Laboratory

Barnacles adhere by secreting a micron-thick proteinaceous layer between themselves and the marine environment that persists throughout their lifespan. These proteins play a dual role in adhering to both the native organism and a foreign substratum, which are often crystalline calcium carbonates from other marine invertebrates, cuticular exoskeleton or sedimentary minerals. Though the sequence and composition of several barnacle cement proteins have been reported, little is known about how these proteins become stably bound to surfaces. Here we use *in situ* atomic force microscopy (AFM) to examine a recombinantly expressed, acidic, calcite-binding 20kDa cement protein, MRCP20. We find that the protein immobilizes on the surface through recognition of distinct atomic steps on the [1014[face of calcite, further assembling on these features into stable nanofibrils. The protein fibrils are continuous and organized at the nanoscale, exhibiting striations with a period of *ca.* 45 nm. The acidic fibrils are also found to manipulate calcite surfaces through the dissolution of underlying calcite features that display the same atomic arrangement. To quantify selectivity, we compare the velocity of atomic steps from calcite etch pits when exposed to water, bulk protein solution, and surface-associated nanofibrils. MRCP20 is found to favor interaction with distinct fast moving steps, where velocity is increased by four- and eight-fold upon exposure to bulk proteins and fibrils, respectively, over steps exposed to solution without protein present. Calcite mineralized in the presence of MRCP20 results in asymmetric crystals, suggesting a similar step-selective behavior by MRCP20 during crystal growth. Cooperative molecular processes with step edge atoms reveal a new regime of biotic interactions with calcite, where specific surface interactions are enhanced through templated long-range nanostructures.

11:40am **BI-WeM12 Thiolene Reaction Applied to Passive Metal Oxide Surfaces for Addressing Protein Adsorption and Cell Adhesion**, ***Anouk Galtayries****, V. Semetey, A. Dellinger*, Chimie ParisTech, France

The aim of this work is to design surfaces allowing controlling biomolecule adhesion by the study of protein adsorption and cell adhesion. In order to answer this challenge,: the optimization of grafting conditions using the thiol-ene reaction of thiol-terminated ethylene glycol (EG) chains (Oligo-

EG or Poly-EG) on a undecenyltrichlorosilane self-assembled monolayer was investigated [1], with the help of surface characterization (angle contact measurement, ellipsometry, fluorescence microscopy, attenuated total reflection infrared *IR-ATR*, X-ray Photoelectron Spectroscopy *XPS*, Time-of-Flight Secondary Ion Mass Spectrometry *ToF-SIMS*) after each reaction step.

Varying different reaction parameters in the methodological investigation of thiol-ene grafting conditions exhibits the development of a bilayer structured system after a 1 minute reaction time as regards OEG grafting, and 1 hour time for PEG grafting. By using different passivated substrates (model silicon single crystal, polycrystalline titanium), different OEG-thiol or PEG-thiol molecules (from 7 to 220 ethylene unit long, methyl-, carboxyl- or amine-terminated), we highlight the range of available versions of this strategy. The terminal chemical functions lead on demand either to protein adsorption inhibition or to biomolecule adsorption, bovine serum albumin (BSA) or fibronectin (Fn) giving access to specific adhesion.

By controlling the light-exposed areas (100 mm-large bands or half-moon surfaces), the photochemistry occurring during the thiol-ene grafting allows to design surface patterning for addressing both protein adsorption and cell adhesion on such sample biointerface on metal oxides.

[1] ``A Facile and Versatile Approach to Design Self-Assembled Monolayers on Glass using Thiol-ene Chemistry", B. Oberleitner, A. Dellinger, M. Déforet, A. Galtayries, A.-S. Castanet,V. Semetey, Chemical Communication, 49, 1615-1617 (2013).

12:00pm **BI-WeM13 Scaling from Single Molecule to Macroscopic Adhesion at Polymer/Metal Interfaces**, ***Thomas Utzig***, *S. Raman, M. Valtiner*, Max-Planck Institut für Eisenforschung GmbH, Germany

Understanding the evolution of macroscopic adhesion based on the fundamental molecular interactions is crucial to design strong and smart polymer/metal interfaces, which play an important role in many industrial and bio-medical applications. Here we show how macroscopic adhesion can be predicted based on single molecular interactions. In particular, we carry out dynamic single molecule force spectroscopy (SM-AFM) in the framework of Bell-Evans' theory to gain information about the energy barrier between the bound and unbound state of an amine/gold junction. Further we use Jarzynski's equality to obtain the equilibrium ground state energy difference of the amine/gold bond from these non-equilibrium force measurements. In addition, we perform Surface Forces Apparatus (SFA) experiments to measure macroscopic adhesion forces at contacts where approximately 10^7 amine/gold bonds are formed simultaneously. The SFA approach provides an amine/gold interaction energy (normalized by the number of interacting molecules) of 36 ± 1 k_BT, which is in excellent agreement with the interaction free energy of 35 ± 3 k_BT calculated using Jarzynski's equality and single molecule AFM experiments. Our results validate Jarzynski's equality for the field of polymer/metal interactions by measuring both sides of the equation. Furthermore, the comparison of SFA and AFM shows how macroscopic interaction energies can be predicted based on single molecular interactions, providing a new strategy to potentially predict adhesive properties of novel glues or coatings as well as bio- and wet adhesion.

Electronic Materials and Processing
Room: 210E - Session EM-WeM

Beyond CMOS: Resistive Switching Devices
Moderator: Christopher Hinkle, University of Texas at Dallas

8:00am **EM-WeM1 Tantalum Oxide Resistive Memory Devices by IAD**, ***Ronald Goeke***, *M. Marinella, D.R. Hughart*, Sandia National Laboratories

Resistive random access memory (ReRAM), or memristors, may be capable of significantly improving the efficiency of neuromorphic computing, when used as a central component of an analog hardware accelerator. However, the current fabrication methods for these nano-ionic resistive memory devices suffer from significant electrical variation within a single device and between devices. This variation degrades the maximum efficiency and accuracy, which can be achieved by a ReRAM-based neuromorphic accelerator.

The switchable resistive thin film at the heart of these memristor devices has been fabricated from sub-stoichiometric tantalum pentoxide using Ion Assisted Deposition (IAD). These devices fabricated with IAD have shown a significant improvement in yield and a big reduction in device performance variability. This success has been repeated many times now. The devices are fabricated from a sub-stoichiometric tantalum pentoxide using IAD to control the oxygen to tantalum ratio. The IAD deposition approach involves e-beam evaporation of tantalum metal with a reactive beam of oxygen and argon ions impinging upon the growing film. Using this technique, the oxide formation occurs at the substrate resulting in good control over film stoichiometry. IAD is a popular technique for the deposition of oxide thin films in the optical coating industry, but has now been demonstrated as a valuable method for growth of oxide electronics. The electrical and optical characterization of these films will be presented.

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

8:20am **EM-WeM2 Capacitance and Resistance Switching in HfO_2 RRAM**, ***Christophe Vallee***, *P. Gonon, C. Mannequin, T. Wakrim, M. Saadi,* LTM, Univ. Grenoble Alpes, CEA-LETI, France*, A. Sylvestre*, G2elab, Univ. Grenoble Alpes, France

This work addresses a new class of electrical devices that could be named "memory impedance", or "MEM-Z" devices. These structures are based on the capability of HfO_2 MIM (Metal – Insulator –Metal) to switch both their resistance and capacitance with a memory effect. Recently, during works led on HfO_2 OxRAM [1], we found that for a specific design, upon voltage biasing, not only does the resistance changes but the capacitance also varies from positive to negative values. In other words, *both the real and imaginary part of the impedance can be controlled by the voltage bias*. If the impedance state can be non-volatile (memory function), then a new class of devices (MEM-Z) can be defined. MEM-Z devices (mem-capacitors and mem-inductors) were recently theorized and their potential applications reviewed [2]: like memristors, they can be used as non-volatile memories, for fuzzy logic (non-binary computing based on continuous variables), and as self-learning devices (neuro-inspired systems, adaptive filters…). They can also be used in tunable electronic circuits such as reconfigurable impedance matching network, reconfigurable amplifiers, programmable filters and oscillators.

In the present work we investigate both resistance and capacitance switching of HfO_2-based MIM device. By comparison to HfO_2 OxRAM, the device has been modified in order to avoid any breakdown during the capacitance switch. Therefore a bi-layer structure is used to obtain a self-compliance MEM-Z device. With this structure a bipolar capacitance cycle has been obtained with decreasing values of capacitance in the ON state. Negative values of capacitance near SET and RESET voltages are also observed. Memory effect for both positive and negative values of capacitance is also demonstrated. At present, the physical origin of capacitance variation is an open question. One hypothesis is that conduction paths, which lead to resistance switching, are the same which lead to capacitance decrease (through the inductive behavior of conduction paths, hopping conduction). This will be discussed in this presentation from the frequency dependence study of the capacitance switch.

[1] P. Gonon, M. Mougenot, C. Vallée, C. Jorel, V. Jousseaume, H. Grampeix, F. El Kamel, "Resistance switching in HfO_2 metal-insulator-metal devices", *Journal of Applied Physics*, vol.107, p.074507 (2010)

[2] Y.V. Pershin, M. Di Ventra, "Memory effects in complex materials and nanoscale systems", *Advances in Physics*, vol. 60, p.145 (2011)

8:40am **EM-WeM3 Density Functional Theory Molecular Dynamics Simulations and Experimental Characterization of high-k/SiGe(110) and SiGe(001) Interfaces**, *A.C. Kummel, E. Chagarov,* University of California at San Diego*, B. Sahu,* Globalfoundries*, S. Oktyabrsky, S. Madisetti,* College of Nanoscale Science and Engineering, Albany-SUNY, ***Tobin Kaufman-Osborn***, University of California at San Diego

Density-Functional Theory (DFT) Molecular Dynamics (MD) simulations were employed to investigate formation at finite temperature of direct interfaces between a-Al_2O_3 oxide and $Si_{0.50}Ge_{0.50}$ substrate with Si- and Ge-terminations. The simulated interfaces revealed mixed bonding between the semiconductor substrate atoms and both O and Al oxide atoms. The oxide/SiGe band gaps were unpinned and close to the SiGe bulk band gap value. The interfaces had SiGe dangling bonds but they were nearly filled and therefore did not produce mid-gap states and could not be passivated by atomic H. The Si terminated surface had a better electronic structure after bonding to oxide compared to the Ge terminated surface since the dangling bonds on the Si atoms tend to be more filled since the Si terminated interface is a better charge acceptor. C-V spectroscopy combined with angle-resolved X-ray photoelectron spectroscopy (AR-XPS) experimentally confirmed formation of interfaces with low interface trap density via direct bonding between a-Al_2O_3 and SiGe.

9:00am **EM-WeM4 Density-Functional Theory Molecular Dynamics Simulations of a-HfO$_2$/Ge(100)(2x1) and a-ZrO$_2$/Ge(100)(2x1) Interface Passivation**, ***Evgueni Chagarov***, University of California at San Diego, *L.M. Porter*, Carnegie Mellon University, *A.C. Kummel*, University of California at San Diego

: The structural properties of a-HfO$_2$/Ge(2x1)-(001) and a-ZrO$_2$/Ge(2x1)-(001) interfaces were investigated with and without a GeOx interface interlayer using density-functional theory (DFT) molecular dynamics (MD) simulations. Realistic amorphous a-HfO$_2$ and a-ZrO$_2$ samples were generated using a hybrid classical-DFT MD "melt-and-quench" approach and tested against experimental properties. The oxide/Ge stacks were annealed at 800K, cooled to 0K, and relaxed providing system with enough freedom to form realistic interfaces. For each high-K/Ge stack type, two systems with single and double interfaces were investigated. All stacks were free of midgap states; however, stacks with an GeOx interlayer had band-edge states which decreased the band gaps by 0-30 %. These band-edge states were mainly produced by under-coordinated Ge atoms in GeOx layer or its vicinity due to deformation, intermixing, and bond-breaking. The DFT-MD simulations show that electronically passive interfaces can be formed either directly between high-K dielectrics and Ge or with a monolayer of GeO$_2$ if the processing does not create or properly passivates under-coordinated Ge atoms and Ge's with significantly distorted bonding angles. Comparison to the charge states of the interfacial atoms from DFT to experimental XPS results show that while most studies of gate oxide on Ge(001) have a GeO$_x$ interfacial layer, it is possible to form a oxide/Ge interface without a GeO$_x$ interfacial layer. Comparison to experiments is consistent with the dangling bonds in the suboxide being responsible for midgap state formation.

9:20am **EM-WeM5 Role of Active and Inert Electrodes in Filament Formation in Resistive Switching Devices (RRAM)**, ***Gargi Ghosh***, Virginia Tech, *S.W. King*, Intel Corporation, *M.K. Orlowski*, Virginia Tech

Reliable filamentary resistive switching (RS) depends largely on the electrochemical properties of the active and inert electrodes. A resistive switching memory cell in a RRAM is generally built as a capacitor-like MIM Cu/TaOx/Pt structure, comprised of an insulating or resistive material sandwiched between two electron conductors. Cu electrode produces via a redox reaction (Cu -> Cu$^+$+e$^-$) highly mobile Cu$^+$ cations that drift in TaO$_x$ and discharge at the inert Pt electrode forming a conductive filament (CF) of the ON state. To assess the role of active and inert electrodes, we report manufacturing and characterization of 4 derivative devices: Cu/TaO$_x$/Ta, Cu/TaO$_x$/Ti, Ta/TaO$_x$/Pt, Ti/TaO$_x$/Pt. For a possible integration of RRAM in CMOS back-end, two new metals Ta and Ti used in CMOS metalization are selected. In all four derivative cells a CF formation could be observed at voltages 2V-5V, comparable with Cu/TaO$_x$/Pt. However, Cu/TaO$_x$/Ti could not be reset, being permanently damaged. Cu/TaO$_x$/Ta could be reset but only a few times displaying noisy reset behavior. Ta/TaO$_x$/Pt device shows resistive switching with a low forming voltage of 2V. The best resistive switching behavior was shown by Ti/Ta$_2$O$_5$/Pt device. Main conclusions of the study: 1) In Cu/TaO$_x$/Ti Cu CFs are formed with a weak base at the Ti electrode due to Cu dissolution in Ti. Cu CF has low resistance and cylindrical shape being difficult to rupture. 2) Cu/TaO$_x$/Ta device shows better switching properties than Cu/TaOx/Ti, because Ta is better diffusion barrier for Cu than Ti. 3) Ta/TaO$_x$/Pt is a potential candidate for RS but suffers from: i) the redox reaction Ta -> Ta$^+$+e$^-$ is much weaker than for Cu, ii) the diffusion of Ta in TaO$_x$ is faster than of Cu in TaO$_x$. The result of these two competing mechanisms are fragile CFs with no resistive constrictions. Hence, the RS is observed but its operation is unreliable. 4) Ti/TaO$_x$/Pt displays if noisy RS. This is due to Ti being known as a getter for oxygen. The Ti CF is therefore fragile as Ti is easily and permanently incorporated in the oxide matrix forming a Ta$_x$Ti$_y$O$_z$ compounds. The overall conclusion from this comparative study is a better understanding of conditions for reliable RS: a metallic filament has to be formed with a resistive constriction, e.g. in the form of truncated cone with a sharp apex. Cylindrical CFs are hard to rupture and hence undesirable for RS. Cone-like CFs for reliable RS require: a) copious supply of metal ions, b) high metal ion diffusivity in the dielectric, c) high ion stopping power of the counter electrode, and d) moderate compliance currents to be applied during the set operation to assure cone-like shape of the CFs.

9:40am **EM-WeM6 Neutron Induced Effects on HfO$_x$-Based Resistive Random Access Memory**, ***Karen Hsu***, *T. Chang*, University of Wisconsin-Madison, *L. Zhao*, Stanford University, *R. Agasie*, University of Wisconsin-Madison, *Y. Nishi*, Stanford University, *Z. Ma, J.L. Shohet*, University of Wisconsin-Madison

As the size of devices decreases and the complexity of electronic chips increases, cosmic-ray-induced crashes are becoming a severe threat to electronic circuits and devices. Resistive Random Access Memory (RRAM) [1], which is considered as a very promising memory technology for embedded systems, has undergone intense research in both industry and academia in the last ten years. As RRAM technology matures and electronic devices using RRAM are likely to be built soon, malfunctions of RRAM will become an important problem in industry since the size of these devices will continue to decrease. Neutrons that come from earth bound or from cosmic ray sources are likely one to produce significant effects on the RRAM [2] based on their fluxes at terrestrial altitudes and their interaction cross sections. In this work, neutrons from the University of Wisconsin Max Carbon Radiation Science Center were used as the radiation source The neutron-induced effects on HfO$_X$ RRAM include single-event-upset (SEU), modification to forming voltage, resistance of both the high-resistance (HRS) and low-resistance states (LRS) and shifts in set/reset voltage.

Some RRAM cells can actually be formed during neutron irradiation and then switch from the HRS to the LRS after additional neutron irradiation. The SEU rate increases linearly as neutron fluence increases. For those neutron-irradiated RRAM cells that did not switch from the HRS to the LRS under irradiation, a smaller forming voltage was required after irradiation. In addition, an increase in the HRS resistance and better switching behavior was observed in those RRAM cells formed entirely by neutron irradiation.

Shifts in the set/reset voltage were also observed after neutron radiation. X-ray diffraction was used on HfO$_2$ films to investigate the physical mechanism, which is attributed to atomic-structure changes in HfOx caused by neutron irradiation.

This work was supported by the Semiconductor Research Corporation under Contract No. 2012-KJ-2359, by the National Science Foundation under Grant No. CBET-1066231.

References:

1. H.-S. Philip Wong, H-Y Lee, S. Yu, Y. S. Chen, Y. Wu, P-S Chen, B. Lee, F. T. Chen, and M-J Tsai, "Metal–oxide RRAM," *Proceedings of the IEEE***100** 1951 (2012).

11:00am **EM-WeM10 Relation of Low-k Interconnect Si-based Dielectric Breakdown to Resistive Switching Behavior**, ***Marius Orlowski***, *G. Ghosh, P. Kassalen, R. Gupta*, Virginia Tech, *S.W. King*, Intel Corporation

The relation between resistive switching (RS) and breakdown and reliability mechanisms are studied for metal-insulator-metal (MIM) structures with low-k dielectrics (SiOC:H, SiCOH, SiNC:H, SiCN:H, SiC:H, SiON:H, SiN:H) all 25 nm thick, with Ti, and Cu as electrode materials that are commonly used in the CMOS back-end process. The TDDB time is correlated with defect generation and related to mechanisms responsible for RS. Defect generation depends exponentially on E$_a$-bxE$_{el}$, where E$_a$ is the activation energy, b is the bond polarization factor being proportional to the molecular dipole moment p$_o$, b=(2+k)/3p$_o$, and E$_{el}$ is the electric field across the dielectric. The breakdown field E$_{bd}$ is determined by E$_a$-bxE$_{bd}$=0, i.e. at high enough electric fields there is effectively no barrier impeding creation of defects. From this condition, the breakdown field E$_{bd}$=E$_a$/b is determined. We obtain, for SiC:H E$_a$=0.28 eV and p$_o$=10e-A, for SiCN:H E$_a$=0.26 eV and b=4e-A, for SiN:H, E$_a$=0.17 eV and p$_o$=1.2eA, for SiON:H p$_o$=1.5e-A. for SiOC:H we obtain E$_a$=1.67eV and p$_o$=15e-A. We find that E$_a$ values of low-k dielectrics are very low compared with those for high-k dielectrics, e.g. E$_a$=4.4 eV for HfO$_2$ with k=21. On the other hand, the strength of the molecular dipole for low-k dielectrics is comparable to that for high-k dielectrics (e.g. p$_o$=11e-A for HfO$_2$). In terms of RS properties under a linear voltage sweep the low-k materials display varied behavior: SiNC:H does not exhibit resistive switching, i.e. under linear voltage stress it shows gradual decrease of resistance but the on-state is volatile, i.e. it evanesces when the cell is unpowered. A similar behavior is observed for SiCN:H, i.e. soft volatile breakdown with a volatile on-state. SiOC:H shows a sharp resistive switching that cannot be reversed - the cell is on permanently. The set voltage is high V$_{set}$=11.8V and it decreases significantly with increasing temperature. SiON:H shows comparable behavior as SiOC:H with slightly lower set voltages. SiC:H shows sharp resistive switching behavior at a moderate set voltage V$_{set}$=6.5V @ 300K. SiN:H displays also a sharp resistive switching but at much higher voltage, V$_{set}$=11.5V @300K. The high set voltages for SiC:H and SiN:H correlate well with high densities of those dielectrics, both at 2.5 g/cm^3 and similar dielectric constant of k=7.2 and 6.5, respectively. The on-state is attributed to the formation of a Cu conductive filaments. The conductive filaments are cylindrical and difficult to rupture. The paper discusses correlation, differences, and commonalities between data obtained for dielectric breakdown and resistive switching mechanisms in terms of the film properties.

11:20am **EM-WeM11 Thin Film Carbon Nanofuses for Permanent Data Storage**, ***Kevin Laughlin***, *S. Jamieson, H. Wang, J. Bagley, T. Pearson, R.C. Davis, M.R. Linford, B.M. Lunt*, Brigham Young University

As memory elements shrink, the reliable life span of digital data is decreasing. Today we all have more data, in less stable formats. For hard drives, DVDs, and flash memory, the reliable life of the data is less than 10 years. Rewriting data extends life, but at high maintenance costs. A potential solution to this challenge is write once read many storage media where writing the data results in a permanent, irreversible change. We have been developing thin film carbon nanofuses for use as a permanent data storage medium. Carbon shows particular promise as an electronic storage medium due to its high localized bond strength resulting in high surface stability and reasonable electrical conductivity. I will present the fabrication and characterization of nanoscale fuses with feature sizes down to ~50nm. The low resistance sp^2 carbon is arc deposited and then patterned using electron beam lithography and plasma etching. The electron beam resist used, HSQ, results in a glass etch mask for pattern transfer into the carbon film with an O_2 plasma. The fuses were written and detected electrically, and excellent stability was observed.

11:40am **EM-WeM12 Low-k/Cu Resistive 2-Level PROM Memory Collocated with CMOS Back-End Metallization**, ***Anshuman Verma***, *G. Ghosh,* Virginia Tech*, S.W. King,* Intel Corporation*, M.K. Orlowski*, Virginia Tech

Building nonvolatile memory directly into a CMOS low-k/Cu interconnects would reduce latency in connectivity constrained computational devices and reduce chip's footprint by stacking memory on top of logic. NVM memory includes two flavors: i) random-access memory, and ii) programmable read-only memory (PROM). The paper investigates suitable choice of materials for an integration of PROM compatible with manufacturing of CMOS back-end. Three capacitor-like MIM structures Al/Ti/I/Cu, with dielectrics I=SiOC:H, SiC:H, SiCN:H, all 25 nm thick, have been selected among samples manufactured by Intel Inc and investigated for resistive switching properties. The samples have been subjected to set and reset operations applied customarily to resistive switching devices with TiAl electrode being grounded and a positive bias applied to Cu electrode. For SiOC:H devices, a sharp transition from R_{OFF}=200MΩ to $R_{ON}(1)$=120kΩ at threshold $V_{set}(1)$= 0.9V - 1.2 V is observed. When the set device is subsequently subjected to a linear voltage ramp, a secondary sharp set transition from $R_{ON}(1)$=120kOhm to $R_{ON}(2)$=2-10Ω is observed at $|V_{set}(2)|$=1.0-1.3V and high compliance currents I_{cc}≈100mA, independent of the bias polarity. $R_{ON}(2)$ can be controlled by the level of I_{cc} (@I_{cc}≈10mA $R_{ON}(2)$=34Ω). Both transitions are irreversible and the low resistance states are stable. The 1st transition is likely to be caused by formation of a Cu conductive filament (CF). Because of the weak diffusion/migration stopping power of Ti for Cu, the resulting Cu CF is of a cylindrical form instead of a conical with the former being very difficult to rupture. The 2nd set transition leads to a dramatic decrease of R_{ON} by a factor 10^5. To ascertain the nature of the CF, we have measured the temperature coefficient of resistance α of the CF and obtain unusually high values, typically α=0.04K^{-1}, which is 10X larger than a for bulk Cu, α=0.0039K^{-1}, or for Cu CF in Cu/TaO_x/Pt, α=0.0033K^{-1}) and 40X higher than a for oxygen vacancy defects CF, α=0.001K^{-1}. The secondary set from $R_{ON}(1)$ to $R_{ON}(2)$ is attributed to some, presently unknown, dramatic phase transformation. Structures with SiC:H (same metal electrodes) show different behavior, but result in the same low resistivity state $R_{ON}(2)$. They require high V_{set}= 3-4V and display volatile behavior at low I_{cc} values. At higher I_{cc} they set into a stable and very low R_{ON}≈5Ω, constituting thus only 1-level PROM. Similarly, devices with SiCN:H are setting permanently only at high I_{cc} currents (50-100mA) and display also very low final resistance of about 10Ω. The paper discusses the properties of the highly conductive, metallic CFs with the uncharacteristically high α.

12:00pm **EM-WeM13 Novel Contact Materials for Reliable Nanoelectromechanical Switches**, ***Frank Streller***, *G. Wabiszewski, D. Durham, R.W. Carpick*, University of Pennsylvania

Nanoelectromechanical (NEM) switches were identified by the roadmap of the semiconductor industry as a low-power "beyond CMOS" technology. However, the reliability of the contact interface currently limits the commercialization of NEM switches, as the electrical contact has to be able to physically open and close up to a quadrillion times without failing, which typically occurs due to adhesion (sticking shut) or contamination (reducing switch conductivity). These failure mechanisms are not well understood, and materials that exhibit the needed performance have not been demonstrated. Thus, commercially viable NEM switches demand the scientific development and characterization of novel contact materials, along with efficient methods to evaluate the interfacial performance of these materials.

We have developed novel contact material candidates that are highly conductive, minimally adhesive, chemically inert, mechanically robust, and amenable to CMOS fabrication processes.[1,2] One promising candidate is platinum silicide (Pt_xSi). The controlled diffusion of sequentially-deposited thin films of amorphous silicon and Pt allowed us to tune the chemical composition of Pt_xSi over a wide range (1<x<3). We measured the mechanical and electrical contact properties of Pt_xSi of multiple stoichiometries in comparison with pure Pt. These experiments showed that the Pt-rich silicide phase (Pt_3Si) may be an ideal contact material for NEM switches due to its desirable combination of mechanical robustness with metal-like conductivity. We also demonstrate that Pt_xSi can be used to release NEM switches with a self-formed gap caused by interfacial separation driven by shrinkage-induced tensile stress.

To assess contact material candidates under NEM switch-like conditions, we developed a novel, high-throughput electrical contact screening method based on atomic force microscopy that enables billions of contact cycles to be tested in laboratory timeframes. We compared the performance of self-mated and dissimilar single asperity Pt and Pt_xSi contacts under forces and environments representative of NEM switch operation, and cycled them up to two billion times. The contact resistance increased by up to six decades due to cycling-induced growth of insulating tribopolymer in the case of Pt-Pt contacts, while Pt_xSi exhibited better stability. Additionally, we found that the original conductivity can be largely recovered by sliding of the contact, which essentially leads to the displacement of the tribopolymer. This suggests a route for mitigating contamination-induced failure.

[1] Streller *et al.*, *Adv. Mater. Interfaces*, 1 (2014).

[2] Streller *et al.*, *IEEE Nanotech. Mag.*, 1 (2015).

Exhibitor Technology Spotlight
Room: Hall 1 - Session EW-WeM

Exhibitor Technology Spotlight Session
Moderator: Dennis Sollon, Kurt J. Lesker

10:20am **EW-WeM8 New and Ongoing Developments in Thin Film Deposition from the Kurt J. Lesker Company®**, *S. Armstrong,* ***Duane Bingaman***, *B. Zinn*, Kurt J. Lesker Company

This presentation will cover the latest developments in deposition sources and PVD and ALD thin film deposition systems. New advances in the field of vacuum deposition science will be outlined with a Q&A session to follow.

10:40am **EW-WeM9 H2O2 Gas: Revolutionary new molecule for ALD**, ***Jeffrey Spiegelman***, *D. Alvarez*, RASIRC

H2O2 is well known for its superior oxidizing capabilities. Now H2O2 is available in high concentration, with or without water and even without carrier gas. H2O2 gas is ideal for next generation materials and 3D architectures that are temperature and water sensitive. Learn about two innovative products that overcome Raoult's Law and deliver stable, repeatable, high concentration H2O2 gas. The Peroxidizer delivers up to 5% H2O2 gas by volume from 30% H2O2 liquid solution. BRUTE Peroxide delivers anhydrous H2O2 gas for water sensitive processes such as ALD involving new materials and 3d architectures.

In-Situ Spectroscopy and Microscopy Focus Topic
Room: 211C - Session IS+AS+SA+SS-WeM

In-situ Studies Using X-ray Absorption Spectroscopy and Vibrational Spectroscopy for Catalytic and Energy Materials
Moderator: Franklin (Feng) Tao, University of Kansas, Zili Wu, Oak Ridge National Laboratory

8:00am **IS+AS+SA+SS-WeM1 *In Situ* X-ray Absorption Spectroscopy Technique for Metal/Water Interface Characterization**, ***Chenghao Wu****, University of California, Berkeley and Lawrence Berkeley National Laboratory*, J.-H. Guo, M.B. Salmeron*, Lawrence Berkeley National Laboratory

Most of the electrochemistry processes occur within the thin layer of electrolyte at the electrolyte/electrode interfaces, commonly denoted as the electrical double layer (EDL). Although some classic continuum theories about EDL have been established and widely accepted over the past century, very little experimental information is available regarding the molecular-level details at such solid/liquid interfaces. We have developed in-situ liquid cells to study such solid/liquid interfaces by means of soft x-ray absorption spectroscopy [1]. Because the fluorescence x-ray photon has much larger mean free path in condensed matters than the secondary electrons, by comparing the total fluorescence yield (TFY) and total

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*** ASSD Student Award Finalist**

electron yield (TEY) spectra, we can extract useful information about the compositional, structural or chemical difference between the bulk and the interfacial electrolyte. Under different bias, by modulating the incident x-ray, the TEY signal current becomes alternating and can be separated from the dominant faradaic current so that we can obtain surface-sensitive TEY signal under electrochemical conditions.

With this *in-situ* and *operando* XAS technique, we investigated the gold/water interface [1] and platinum/sulfuric acid solution interface. It was found that at gold/water interface, the interfacial water layer has significantly different hydrogen-bonding network structure compared to the bulk water. Under different bias, the polar water molecules respond to the external electrical field and reorient at the gold electrode surface, which significantly changes the amount of distorted or broken hydrogen bonds. First-principle simulations were able to corroborate the experimental results and qualitatively reproduce the change in the x-ray absorption spectra at different bias. In the platinum/sulfuric acid system, the charged solute species, such as SO_4^{2-} ions, hydronium ions, introduce extra complexity at the surface under different bias. Using the same *in-situ* technique, we were also able to identify some intermediate surface species in the potential window of OER reaction.

[1]. J.J. Velasco-Velez, C.H. Wu, T.A. Pascal, L.F. Wan, J.-H. Guo, D. Prendergast, and M. B. Salmeron, *Science*, **346**, 831-834 (2014).

8:20am IS+AS+SA+SS-WeM2 Tip Enhanced Raman Spectroscopy (TERS) of Graphene Nano-Ribbons and Graphene on Au Surfaces: Imaging and Vibrational Spectroscopy of Surface Reaction Products

Delroy Baugh, *S. Liu, T. Kumagai, M. Wolf*, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

Tip Enhanced Raman Spectroscopy (TERS) is currently one of the most powerful probe techniques available and could be used to study reactions on surfaces at the single molecule level. TERS combines two very well developed techniques scanning probe microscopy (SPM), used to image single molecules on surfaces, and surface enhanced Raman spectroscopy (SERS), used to characterize vibrational spectra also of single molecules on surfaces. TERS could therefore provide unique and heretofore unprecedented insight on adsorbate reactions at the single-molecule level, e.g., image a molecule while it evolves from reactant to product at well defined surface sites as well as monitor vibrational spectra to provide bond specific information about the reaction. However, in order to clarify the vibrational structure in TERS, the details of the enhancement mechanism and the issues regarding the plasmonic background that is almost always observed in TER spectra as well the “blinking” that occurs in the SERS part of TERS must be resolved. Towards this end here we will report studies of Graphene and Graphene Nanoribbons (GNR’s) on Au surfaces as a model systems because their electronic and vibrational structure are clearly defined. Specifically, Near and Far-field Raman spectra will be reported for these systems and the above issues will be addressed experimentally and a simple theoretical model will be presented for the TERS observations.

8:40am IS+AS+SA+SS-WeM3 Isomerization of One Molecule Observed through Tip-Enhanced Raman Spectroscopy: Azobenzene Thiol on Au(111)

Joonhee Lee, *N. Tallarida, L. Rios, V.A. Apkarian*, University of California, Irvine

The reversible *cis-trans* isomerization of a single azobenzene thiol (ABT) molecule is captured in tip-enhanced Raman trajectories in which the anti-correlated flip-flop between discrete, on and off-states of the two structural isomers is seen. The strongly blue-shifted spectra are recorded from a molecule that appears at the junction plasmon of a scanning tunneling microscope (STM), consisting of an atomically flat Au(111) surface and a silver tip. The variation in frequencies of switching events identifies heterogeneously photocatalyzed chemistry. The chemisorbed ensemble of ABT molecules lie flat on Au(111) surface with azobenzene headgroup strongly coupled to the surface. Nevertheless, we establish through STM imaging that the ABT molecules undergo both current driven and photoinduced *cis-trans* isomerization. Rather than decoupling from the surface, we suggest that strong coupling of the reaction coordinate to a vibrational energy sink is required for *cis-trans* isomerization of azobenzenes on metal surfaces.

9:00am IS+AS+SA+SS-WeM4 *In Situ* Characterization and Reaction Studies of MnO_x/Co_3O_4 Catalyst for CO and CO_2 Conversion

Walter Ralston, *G. Melaet,* University of California, Berkeley, *S. Alayoglu,* Lawrence Berkeley National Laboratory (LBNL), *G.A. Somorjai*, University of California, Berkeley

As the energy and fuel demands of our growing world continue to increase, non-fossil fuel carbon sources are increasingly attractive – especially if these carbon sources can be easily converted to transportable fuels and higher-value chemicals. Much attention has been focused on carbon dioxide, as capture and storage technology has emerged to mitigate emissions and CO_2 can be used to produce methanol.

Recently, we reported a catalyst for the low-pressure conversion of CO_2 to methanol[1]. Manganese oxide nanoparticles supported in mesoporous Co_3O_4 produced methanol in high yields and at significantly lower pressure conditions than typical Cu/ZnO catalysts used industrially. The advantage of this catalyst is in its lower pressure requirement, its high yield of methanol, and its evidence of carbon-carbon bond formation (10% ethylene production).

Catalytic testing of the material has shown the catalyst to be more than the sum of its parts; when each component is tested separately (MnO_x nanoparticles supported in SiO_2; mesoporous Co_3O_4 alone) CH_4 and CO are the major products. Preparation and testing of an inverse catalyst – CoO_x nanoparticles on a mesoporous MnO_2 support – proves the importance of the hybrid architecture in determining the selectivity of the catalyst, as the inverse catalyst is dominated by the selectivity of the support (>80% selective to CO).

Towards understanding this catalyst, in-situ X-ray Absorption Spectroscopy (XAS) utilizing both soft and hard x-ray energies has allowed for a detailed characterization of the catalyst under oxidation, reduction, and reaction conditions. In addition to CO_2, in-situ characterization under CO hydrogenation conditions was used to understand the Fischer-Tropsch activity of the catalyst for making longer chain hydrocarbons. The results of these in-situ studies are correlated with catalytic reaction data to help understand the nature of the active site/interface and guide future catalyst design.

References

(1) C. S. Li, G. Melaet, W. T. Ralston, *et al.* High-performance hybrid oxide catalyst of manganese and cobalt for low-pressure methanol synthesis. *Nature Communications,* 6:6538, **2015**.

9:20am IS+AS+SA+SS-WeM5 *In Situ* and *Operando* Raman Methodology to Understand the States of Oxide Catalysts and Alkane Oxidative Dehydrogenation and Ammoxidation Reactions

Miguel A. Bañares, Instituto de Catálisis y Petroleoquímica, Madrid **INVITED**

Operando methodology combines in situ spectroscopy during reaction with simultaneous performance measurement in a cell that behaves like a catalytic reactor. *Operando* methodology connects changes in the performance and in the structure in a simultaneous manner; this is fundamental to assess the structure-performance relationships at a molecular level.

Molecularly dispersed vanadia on oxide carriers is a key component in many catalytic formulations in environmental and selective oxidation and ammoxidation catalysis. The actual state of vanadia catalysts in specific environments depends on its surface density, the nature of the support and the presence of additives. We will summarize our experience on the state of supported vanadia paying particular attention to how the environment and reaction conditions finally shape the structure of vanadia catalysts. O*perando* Raman spectroscopy is an invaluable approach to fully understand the actual state of the catalyst, its transformations during reaction and how these correlate with changes in catalytic performance.

A single technique, may no deliver the complete vista, thus collaboration with complementary talents and techniques is critical. We show the outcome of collaborations with theoretical chemistry approaches to bring the rationale behind structure-activity relationships inferred through *operando* Raman methodology. We also show the interaction with engineering approaches.

11:00am IS+AS+SA+SS-WeM10 *Operando* Studies of Dynamic Restructuring of Working Catalysts by Correlated Imaging and Spectroscopy Probes

Anatoly Frenkel, Yeshiva University **INVITED**

Understanding mechanisms of reactivity is often hindered by complexity of nanoscale supported metal catalysts. In the size range of 1-5nm, they feature a variety of structural motifs, sizes, shapes, compositions, degrees of crystalline order as well as multiple temporal scales. Hence, new experimental methodologies are called for, ones that are capable to capture not only the details of kinetic, dynamic and catalytic properties of metal clusters, but also their statistical distributions over ensemble of such clusters in a particular working catalyst, i.e., in reaction conditions. I will present our recent results obtained at the National Synchrotron Light Source, Advanced Light Source and Center for Functional Nanomaterials, where we combined x-ray absorption spectroscopy, high resolution transmission electron microscopy and micro-IR spectroscopy studies of a complex catalytic system *in operando*, using the same portable micro-reactor. This method will be illustrated on the example of supported Pt and Pd catalysts undergoing dynamic restructuring during ethylene hydrogenation reaction. Our results demonstrate a complexity of structures exhibited in this system and their dynamic, responsive transformations throughout changing reaction conditions. The new method is both general and generalizable to quantitative *operando* studies of complex material systems of broad interest to areas as diverse as catalysis science, applied physics and materials science, using a wide variety of x-ray and electron based experimental probes.

11:40am **IS+AS+SA+SS-WeM12 A Correlation of Raman and Single and Multiple Layer Graphene Conductivity as Detected with a Cryogenic Multiprobe AFM with On-line Raman, NSOM and Other SPM Modalities**, ***Aaron Lewis***, The Hebrew University of Jerusalem and Nanonics Imaging Ltd, Israel, *O. Zinoviev, A. Komissar, E. Maayan, D. Lewis*, Nanonics Imaging Ltd, Jerusalem, Israel

It is a challenge to study 2D materials, such as Graphene, MoS_2, $WeSe_2$, etc. at temperatures down to 10^oK when one considers the wide variety of physical phenomena that have to be applied to get a full picture of the functionality of these materials. This involves questions of structure, nanometric photoconductivity, electrical properties, thermal properties, near-field optical in the apertured and scattering modes, Kelvin probe, and of course Raman. All of these phenomena are common not only to 2D materials but also to carbon nanotubes and related nanomaterials. This presentation will describe both the instrumental development of such a multiprobe cryogenic system that allows for state of the art on-line optical measurements and will also include a review of the probe developments that permit such multifunctional multiprobe operation with on-line full optical access. The system that will be described has a completely free optical axis from above and below that is not obscured by electrical or other probes that have been developed for this system for multiprobe operation. This permits on-line Raman and Tip Enhanced NanoRaman Scattering. With such a system we have investigated graphene and HfO2 using multiprobe electrical, Kelvin probe, NSOM and on-line Raman. The results have yielded new insights into the chemical changes that are correlated to the electrical conductivity.

12:00pm **IS+AS+SA+SS-WeM13 Surface Structure and Chemistry of Rh(110)-1×2 Under Reaction Condition and During Catalysis explored with AP-XPS and HP-STM**, ***Franklin (Feng) Tao***, *L. Nguyen*, University of Kansas

High pressure scanning tunneling microscopy (HP-STM), ambient pressure X-ray photoelectron spectroscopy (AP-XPS), and computational studies were used to study the surface chemistry and structure of Rh(110)-1×2 and Rh(110)-1×1 at atomic scale in CO at different pressure and different temperature, and during CO oxidation at different pressure and different temperature. In gas of CO at a low pressure of 8×10^{-8} Torr, a Rh(110)-1×2 covered with CO is formed at 25C by replacing the adsorbed oxygen atoms adsorbed on Rh(110)-1×2 by CO molecules of gas phase. A pressure dependent structure of adsorbate layer of CO on Rh(110)-1×2 was revealed. In gas of CO at a high pressure of 0.08 Torr, the portion of CO molecules bound in atop configuration in the adsorbed layer increases along with the increase of pressure of CO gas though there is no restructuring of Rh(110)-1×2 at 25C in the pressure range of 8×10^{-8} to 0.8 Torr. This is supported by the calculated coverage-dependent binding energy of CO on this surface. At a relatively high temperature of 55C, Rh(110)-1×2 in 0.08 Torr CO is restructured to Rh(110)-1×1 (Figure 1b). This temperature of surface restructuring is much lower than 153C for Rh(110)-1×2 in UHV. Theoretical simulation suggests that adsorbed CO molecules promote this restructuring compared to the restructuring in UHV since adsorption of CO on the intermediate structures of this restructuring in gas of CO lower the activation barrier of these intermediate structures. Rh(110)-1×2 is restructured to Rh(110)-1×1 during catalysis in the mixture of CO (0.08 Torr) and O_2 (0.02 Torr) even at 25C. Compared to the lack of restructuring in pure CO of 0.08 Torr at 25C, this restructuring during catalysis could result from a local heating of the catalyst surface by the exothermic reaction of CO oxidation. During CO oxidation, certain number of CO molecules are still remained on the catalyst surface. In the temperature range of 50-130C the active phase of catalysis is metallic Rh(110)-1×1. However, at 200C the active phase is surface rhodium oxide. These in-situ studies of surface structure and chemistry integrated with computational studies of Rh(110) in pure CO and in mixture of CO and O_2 clearly demonstrate the complexity of surface structure of a catalyst under reaction condition and during catalysis. The pressure-dependent structure of adsdorbate layer, temperature-driven surface restructurings, generation of a new active surface phase of catalyst during catalysis, suggest the significance of in-situ studies of structure and chemistry of surface of a catalyst during catalysis.

MEMS and NEMS
Room: 211A - Session MN+AM-WeM

Emerging Materials & Fabrication Technologies toward Scalable & Additive Nanomanufacturing I
Moderator: Philip Feng, Case Western Reserve University, Roya Maboudian, University of California at Berkeley

8:00am **MN+AM-WeM1 The Why, the What and the How of Nanomanufacturing**, ***Khershed Cooper***, National Science Foundation (NSF) **INVITED**

In 2010, at the conclusion of the review of the NNI, PCAST recommended greater emphasis on commercialization by doubling investment of the Federal Government in nanomanufacturing R&D. Federal agencies responded in various ways. The NNI Signature Initiative: Sustainable Nanomanufacturing was announced, OSD's MURI topic call included nanomanufacturing as a high-priority theme, and NSF announced the Scalable Nanomanufacturing solicitation. The private sector also responded to the need for nanotechnology commercialization through interest groups such as the NanoBusiness Alliance and, as the Institutes for Manufacturing Innovation multiply, nanoscience and nanotechnology appear to play an increasing important role. This is the 'why' of nanomanufacturing. Nanomanufacturing is the fabrication of nano-scale building-blocks, their assembly into higher-order structures and the integration of these into larger scale systems such that both heterogeneity and complexity are achievable with manipulation and control at the nano-scale. R&D activities address the nanomanufacturing value chain and manufacturability challenges such as scale-up and cost. This is the 'what' of nanomanufacturing. This talk will discuss these aspects of nanomanufacturing and 'how' the nanomanufacturing programs (NM, SNM, NSEC, NERC, SBIR) at NSF are meeting these challenges through support of basic and applied research involving novel ideas. Proposed ideas encompass a wide range of materials, processes and applications and are usually based on strong fundamental foundations. Research outputs are nanomanufacturing fundamentals that will help overcome barriers to large-scale, high quality production of nano-enabled products for the benefit of society.

8:40am **MN+AM-WeM3 Large-Area Nanoimprinting and Nanoplasmonics for Energy Harvesting, LEDs & Biosensing**, ***Stephen Y. Chou***, Princeton University **INVITED**

This talk will present (1) the technology advances and applications of nanoimprinting, a revolutionary nanofabrication method that not only allows the fabrication of nanostructures that could not be fabricated before, but also offers a viable way to mass manufacturing of nanostructures and hence commercialization; and (2) new nanoplasmonic structures for high efficiency solar cells and LEDs and ultrasensitive biosensing that have unprecedented properties and performances.

In nanoimprint, the presentation will address the advances in (a) planar as well as roll-to-roll nanoimprinting, (b) methods of making large nanostructure nanoimprint molds without using direct-write (e.g. electron-beam lithography), (c) self-perfection technologies, and applications in electronics, optics, optoelectronics, magnetics, biotechnologies, displays, and energy harvesting.

In nanoplasmonics, the presentation will discuss the advances in design large-area, high performance nanoplasmonics used for solar cell, LEDs and biosensing, in particular, two new nanoplasmonic structures: disk-coupled dots-on-pillar antenna-array (D2PA) and plasmonic cavity with subwavelength hole-arrays (PlaCSH). Significant enhances in energy efficiency and detection sensitivity have been achieved using D2PA and PlaCSH.

9:20am **MN+AM-WeM5 Scalable Nanomanufacturing of Plasmonic and Metasurfaces**, ***Regina Ragan***, *F. Capolino*, University of California Irvine **INVITED**

Nanodisks and nanoparticles serve as meta-molecule building blocks to tune plasmonic and metamaterial properties when arranged in planar and three-dimensional geometries. For example, the ability to control nanomaterial interfaces via colloidal synthesis allows for tuning of the plasmon resonance as well as mitigating losses affecting extinction spectra. In addition, colloidal assembly is beneficial as a high-throughput, wafer scale deposition method. We have achieved robust surface enhanced Raman scattering (SERS) sensors approaching single molecule detection limits *reproducibly* over large areas using colloidal assembly. Transmission electron microscopy data shows that by varying driving forces for assembly, diffusion versus electrophoresis, nanoparticle clusters with gaps between nanoparticles of 4 nm down to 1 nm, respectively, are obtained. Corresponding orders of magnitude decreases in detection limit allow for identification of fermentation products present in the parts per billion range in cystic fibrosis patients.

Arrays of tightly coupled metal and metal- dielectric nanoparticles also support narrow band resonances, Fano resonances, based on "dark" electric and/or magnetic resonances. We will discuss how material interfaces can be used to mitigate losses that eliminate Fano resonant features. For example, the extinction and absorption efficiencies resulting from an array of linear trimers of Au nanoshells in homogeneous environment show that efficiency is affected by changing dye concentration in nanoshells. The use of dyes as gain media induces sharpened Fano resonance features (attributed to the meta-molecule nature of the linear trimers) and increased maximum absorption efficiency at 422 THz. Using similar methods, circular nanoclusters (CNC) of metal nanoparticles can support a magnetic Fano resonance at 472 THzvia dipole moments forming a current loop underoblique TE-polarized plane wave incidence. In particular, array-induced resonances are narrower than single-CNC-induced ones and also provide even larger field enhancements, in particular generating a magnetic field enhancement of about 10-folds and an electric field enhancement of about 40-folds for a representative metasurface.Natural magnetism fades away at infrared and optical frequencies and artificial magnetism is cumbersome to achieve in these regimes, as conventional split ring resonators are difficult to scale down to optical wavelengths. Nanoparticles assembled from colloids are a scalable approach to engineer materials' electromagnetic properties.

11:00am **MN+AM-WeM10 Roll to Roll Processes at the University of Michigan: Continuous Patterning, Flexible OPVs, and Growth of Carbon Nanomaterials***, **Jay Guo***, University of Michigan, Ann Arbor **INVITED**

Roll to roll fabrication is regarded as a high-throughput and cost-effective method for future manufacturing of flexible electronics, large area photonic elements and functional surfaces for a variety of applications. This talk will discuss a few examples of roll to roll processes developed at the University of Michigan. First, roll-based patterning processes will be introduced. These include roll to roll nanoimprint lithography (R2RNIL) based on mechanical deformation of polymers and capable of tens of nm resolution, photo-roller-lithography (PRL) by using flexible photomasks to pattern sub-micron and larger features continuously on a moving web. These techniques can be used in many applications, such as metal wire grid based transparent conductors. Next, fabrication of organic optoelectronics OLED and OPV by roll to roll coating processes such as blade coating, blade-slit coating will be discussed. The coating process should be selected properly by considering the thickness requirement for each active layers in the devices. Finally I will report some progress made by the UM team in the Scalable NanoManufacturing program in the roll based continuous growth of carbon nanotubes and graphene.

11:40am **MN+AM-WeM12 Nanotube Templated Manufacturing of Hierarchically Structured High Throughput Fluid Filters***, **Andrew Davis**, R.C. Davis, R. Vanfleet,* Brigham Young University*, N. Morrill,* Precision Membranes

High throughput microfilters for use in water purification have been developed to address filtration challenges by dramatically decreasing flow resistance and filter size while improving filter strength, longevity, and affordability. The microfilters were fabricated out of a high strength carbon-nanotube composite material using a process for precise hierarchical patterning on both the micro and nano scales.

12:00pm **MN+AM-WeM13 Improved Vacuum Deposition of Small Patterned Features Using Precision Shadow Masks and a Novel Low Pressure Sputtering Source***, **Rob Belan***, Kurt J. Lesker Company*, V. Heydemann,* Advantech U.S. Inc*, S. Armstrong,* Kurt J. Lesker Company*, T. Fisher, B. Brocato*, Advantech U.S. Inc

A novel, low pressure sputter source has been used in conjunction with a precision shadow mask to deposit crisp features on glass substrates. The low pressure sputter source (LPSS) exhibits high-rate omnidirectional deposition and can form crisp lined features that are typically 5 µm to 50 µm in size when combined with precision mask technology. These feature sizes are a factor of 5x smaller compared to traditional magnetron sputtering at typical sputtering pressures (~1 Pa). The LPSS operates at pressures lower than 0.1 Pa which increases the mean free path of the sputtered atoms and reduces the spread of the deposited pattern through a shadow mask that is often associated with magnetron sputtering at normal pressures.

The LPSS sputters at rates (up to 3 Å/s) with precise rate control in the range of 1 Å/s to 3 Å/s for target/substrate distances from 76 mm to 101 mm. The first generation LPSS utilized a 137 mm x 5.4 mm aluminum cathode. The second generation LPSS employed a 826 mm x 32.5 mm high purity (10 ppm) aluminum cathode demonstrating the scalability of this novel deposition source.

Patterned thin films with thicknesses between 300 Å to 2,000 Å were deposited using the first and second generation low pressure sputter sources. The impact of ambient pressure, power and source/substrate distance on the resulting thin film was investigated. The deposition runs were conducted under static conditions, with stationary source and substrate, as well as with a scanning source.

Patterned features were deposited on display-grade borosilicate glass substrates by placing custom manufactured nickel shadow masks with apertures in the 20 µm to 50 µm size range between the low pressure sputter source and the substrates. The shadow masks are manufactured by an electroforming process that allows precise control of the mask thickness. Typical shadow mask materials are nickel and invar (FeNi36). As well as studying the sputtering process parameters of the LPSS the quality of the deposited patterned features were investigated using a variety of mask thicknesses and aperture dimensions.

The low pressure operation of the LPSS source enables thin film deposition of precision nanostructured patterns via shadow masks and sputtering, an area traditionally kept to evaporation methods. Results and conclusions of this work will be presented for this emerging fabrication technology.

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.

Reference:

(1) Toyli, D. M.; Christle, D. J.; Alkauskas, A.; Buckley, B. B.; Van de Walle, C. G.; Awschalom, D. D. Measurement and control of single nitrogen-vacancy center spins above 600 K. *Phys. Rev. X.***2012**, *2*, 031001.

(2) Loza, P.; Kouznetsov, D.; Ortega, R. Temperature distribution in a uniform medium heated by linear absorption of a Gaussian light beam. *Appl. Opt.***1994**, *33*, 3831–3836.

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 mixutures 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 ^{o}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.

References:

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3. Fukushima, T.; Kosaka, A.; Ishimura, Y.; Yamamoto, T.; Takigawa, T.; Ishii, N.; Aida, T. *Science* **2003,***300*, 2072.
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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.

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Plasma Science and Technology
Room: 210B - Session PS+2D+SE-WeM

Plasma Diagnostics, Sensors and Control II
Moderator: Colin Wolden, Colorado School of Mines

8:20am **PS+2D+SE-WeM2 Diagnostics for Ionized Physical Vapor Deposition Chambers**, ***YuiLun Wu****, P. Piotrowicz,* University of Illinois at Urbana-Champaign*, I.A. Shehelkanov,* National Nuclear Research University (MEPhI)*, D.N. Ruzic*, University of Illinois at Urbana-Champaign

As the critical dimension of the semiconductor device continues to shrink and aspect ratio continues to rise, more diagnostics are needed to accurately predict the deposition profile of features on the wafer. Traditionally, the incident ion fluxes are considered to be perfectly normal to the wafer plane due to the electric field of the plasma sheath. However from simulation results [1] the ion flux from a magnetron discharge has a narrow angular distribution and this distribution is becoming more significant as the aspect ratio increases. In order to confirm and adjust this predicted distribution a sensor to measure angular distribution of ions in an industrial scale chamber is designed and developed. The sensor is a combined gridded energy analyzer (GEA) and a quartz crystal microbalance (QCM) [2], with a high aspect ratio collimator in place of the normal electron repeller grid for angular measurement distribution measurements. The collimator is made of 3D-printed plastic elements with 600µm nominal openings which provides 1 degree angular resolution. This combined QCM and GEA setup is capable to determine fluxes of metal ions, metal atoms and argon ions at 30kW DC magnetron nominal target power. The setup is able to tilt around 10 degrees about the wafer plane in 1 degree intervals and measure the angular distribution of the ion and neutral fluxes generated by the discharge. A time resolved triple Langmuir probe was also employed to measure the plasma parameters such as electron temperature and density and scanning in a three dimensional map.

References:

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8:40am **PS+2D+SE-WeM3 Probing the Plasma Chemistry that Underpins Diamond Chemical Vapour Deposition**, ***Michael Ashfold***, University of Bristol, United Kingdom of Great Britain and Northern Ireland, *M.W. Kelly, B.S. Truscott,* University of Bristol, UK, United Kingdom of Great Britain and Northern Ireland, *Y.A. Mankelevich*, Moscow State University, Russia, Russian Federation **INVITED**

Most diamond chemical vapour deposition (CVD) employs microwave (MW) activated C/H (typically CH_4/H_2) gas mixtures. Many previous studies have sought to explore (and optimise) radical formation in such activated gas mixture, and the ways in which these radicals add to, and are accommodated on and in, the growing diamond surface.

Our activities in this area employ an interrelated three-pronged approach, *i.e.*

i) electronic spectroscopy methods (cavity ring down absorption and optical emission spectroscopies) to determine the spatial distributions of selected species (*e.g.* H atoms, CH and C_2 radicals) as functions of process variables like the process gas mixing ratio, flow rate and total pressure, and MW power,

ii) complementary 2-dimensional (2-D) modelling of the plasma chemistry and composition with the aim not just of rationalising the spatial resolved column density data obtained in (i), but also enabling prediction of the concentrations of other key gas phase species (*e.g.* CH_3 radicals, which are generally regarded as the dominant growth species) that are not amenable to spectroscopic detection, as functions of process condition, and

iii) quantum mechanical (QM) and QM-molecular mechanics (MM) calculations of the energetics of the elementary steps involved in radical addition to, migration on, and eventual accommodation on, a growing diamond surface.

This invited presentation will summarise the current understanding of diamond CVD from traditional C/H gas mixtures and results of recent studies designed to explore and explain the significant growth rate enhancements that can be achieved by adding trace amounts of nitrogen to such gas mixtures.

9:20am **PS+2D+SE-WeM5 Ionization Zones and the Deposition of Thin Films in the Transition Region from Non-Reactive to Reactive Magnetron Sputtering including dc, HiPIMS, and Burst-HiPIMS Modes**, ***Yuchen Yang***, *X. Zhou, A. Anders*, Lawrence Berkeley Lab, University of California, Berkeley

Research has been done for copper and chromium targets in conventional non-reactive HiPIMS, revealing the disappearance of localized ionization zones when operating at high power due to high metal neutral supply from the target. However, relatively little research has been done for reactive HiPIMS. In this work we investigate the existence of ionization zones in various forms of reactive magnetron sputtering: direct current (dc) and HiPIMS for conventional pulse patterns and in burst mode. Copper and chromium targets are selected with nitrogen as reactive gas because (i) in the non-reactive regime Cu and Cr can be operated with or without ionization zones, and (ii) these target materials form application-relevant compound films, e.g. of interest in wear and corrosion-resistant applications, medical implants, metallization layers, etc.

Work at LBNL is supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

11:00am **PS+2D+SE-WeM10 Modelling of the Reactive High Power Impulse Magnetron Sputtering (HiPIMS) process**, ***JonTomas Gudmundsson***, University of Iceland, *D. Lundin,* Université Paris-Sud, France, *N. Brenning,* KTH Royal Institute of Technology, Sweden, *T. Minea*, Université Paris-Sud, France

Reactive high power impulse magnetron sputtering (HiPIMS) [1] provides both a high ionization fraction of the sputtered material and a high dissociation fraction of the molecular gas. We demonstrate this through an ionization region model (IRM) [2] of the reactive Ar/O_2 HiPIMS discharge with a titanium target that was developed to study the temporal behavior of the discharge plasma parameters. We explore the influence of oxygen dilution on the discharge properties such as electron density, the ionization fraction of the sputtered vapour, the oxygen dissociation fraction and the onset and role of self sputtering. We discuss the important processes and challenges for more detailed modeling of the reactive HiPIMS discharge. Furthermore, we discuss experimental observations during reactive high power impulse magnetron sputtering sputtering (HiPIMS) of Ti target in Ar/N_2 and Ar/O_2 atmosphere. The discharge current waveform is highly dependent on the reactive gas flow rate, pulse repetition frequency and discharge voltage. The discharge current increases with decreasing repetition frequency. This we attribute to an increase in the effective secondary electron emission yield during the self-sputtering phase of the pulse, as nitride [3] or oxide [4] forms on the target.

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11:20am **PS+2D+SE-WeM11** ***Pulsed Magnetron Sputtering Plasma Optimization for Large Area Growth of Two-dimensional MoS_2*****,** ***Andrey Voevodin***, Air Force Research Laboratory, *C. Muratore,* University of Dayton, *A.R. Waite, J. Bultman, A. Safriet, J. Hu*, Air Force Research Laboratory

Pulsed magnetron sputtering process provides and alternative scalable and reduced temperature growth pathway for the direct synthesis of two-dimensional (2D) materials for electronic device applications [1]. To avoid defect generation by excessive ion bombardment, while maintaining sufficient adatom mobility on the condensation surface at low substrate temperatures, the ion flux and kinetic energy must be modulated. In this study a variable intensity magnetic field was used to control chemistry, energy, and spatial density distribution characteristics of plasma produced by pulsed magnetron sputtering of MoS_2 in 15 mTorr argon. An electromagnetic coil positioned above the substrate generated a 5-15 G magnetic field near substrate surface, causing redirection of magnetron particle flux for tuning of electron and ion densities at the substrate surface. Both plasma emission and mass-spectroscopy analysis showed an abundance of excited and ionized Ar as well as Mo and S species with no evidence for MoS radicals. Wavelength specific plasma imaging and mass/energy spectroscopy studies demonstrated that the applied magnetic field mostly affects excited and ionized Ar generated in background gas collisions with electrons trapped by the magnetic field lines, while the trajectories of Mo and S species generated from the target surfaces are influenced to a much lesser degree. The imposed magnetic field intensity was adjusted to selectively filter Ar species from reaching the substrate and to find a balance between reducing unnecessary Ar bombardment and preventing shifting energy distributions of all arriving ions above 8 Ev, where point defect generation is expected for hexagonal MoS_2. Plasma studies were used to select optimum growth conditions for 2D MoS_2 synthesis on SiO_2 surfaces at 700 ^{0}C. Film thickness uniformity was verified by producing 2-3 monolayer layer thick hexagonal polycrystalline MoS_2 films over 25-50 mm scale area sizes as confirmed by in-situ Raman spectroscopy and TEM microscopy.

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11:40am **PS+2D+SE-WeM12 Molybdenum Nitride Formation by N_2 Plasma Exposure on Molybdenum Disulfide: In-situ Surface Study**, ***Angelica Azcatl***, *X. Qin, Q. Wang, N. Lu, M.J. Kim, C.L. Hinkle, R.M. Wallace*, The University of Texas at Dallas

Two-dimensional molybdenum disulfide (MoS_2) is currently considered as a potential channel material for CMOS applications. Electron mobilities on the order of 470 cm^2/Vs [1] have been reported for few-layer MoS_2 based FETs. Such promising results have fueled the efforts on synthesis of large area and high quality mono and few-layer MoS_2. Yet, the development of MoS_2 processing techniques of interest for device fabrication (i.e. doping, etching, functionalization) is still in an early stage.

Recently, it has been reported that when MoS_2 is exposed to SF_6, CF_4 or CHF_3 plasma treatments, fluorine can be introduced in the MoS_2 structure as an acceptor dopant, resulting in p-type doping. In parallel, due to the weak van der Waals interlayer forces, layer etching occurred as a side effect after these fluorine-based plasma exposures. [2]

Following the exploration of the effect of plasma exposures on MoS_2, in this study nitrogen plasma exposures on MoS_2 were performed, while the surface chemistry was monitored by in-situ by X-ray Photoelectron Spectroscopy. Theoretical studies have shown that substitution of sulfur with nitrogen in MoS_2 leads to p-type doping. [3,4] Here, the chemical analysis obtained by XPS indicates that nitrogen will covalently interact with molybdenum to generate molybdenum nitride. It was found that the nitrogen content in MoS_2 can be controlled with exposure time. The thermal stability of MoN_x formed due to sulfur replacement with nitrogen will be discussed. Finally, Raman Spectroscopy studies and Scanning Transmission Electrons Microscopy imaging on the MoN_x/MoS_2 structure will be presented to discuss the impact of the Mo-N bonding environment on the MoS_2 structure. This study will give an important insight for the understanding of the interaction of MoS_2 with a non-metal dopant atom, nitrogen, which has implications on the electrical properties of MoS_2.

This work is supported in part the Center for Low Energy Systems Technology (LEAST), one of six centers supported by the STARnet phase of the Focus Center Research Program (FCRP), a Semiconductor Research Corporation program sponsored by MARCO and DARPA, and by the SWAN Center, a SRC center sponsored by the Nanoelectronics Research Initiative and NIST.

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12:00pm **PS+2D+SE-WeM13 Low Temperature Synthesis of $AlYB_{14}$ by High Power Pulsed Magnetron Sputtering**, ***Oliver Hunold***, *Y.T. Chen, D. Music,* RWTH Aachen University, Germany, *P.O.A. Persson,* Linköping University, Sweden, *J.M. Schneider*, RWTH Aachen University, Germany

The influence of ion bombardment on the structure evolution of $AlYB_{14}$ was studied by using high power pulsed magnetron sputtering (HPPMS). The structure was analyzed by X-ray and electron diffraction. The diffraction data are consistent with the formation of crystalline $AlYB_{14}$ domains in an amorphous matrix. As the growth temperature was 675 °C synthesis was conducted at 725 °C below the bulk synthesis temperature. It is reasonable to assume that this decrease in the growth temperature is facilitated by bombardment of ions formed in the HPPMS discharge resulting in enhanced surface diffusion and hence higher adatom mobility. This work may be relevant for synthesizing other boron rich solids with low symmetry crystal structures at temperatures well below their bulk synthesis temperature.

Plasma Science and Technology
Room: 210A - Session PS+SS+TF-WeM

Atomic Layer Etching (ALE) and Low-Damage Processes I
Moderator: Geunyoung Yeom, Sungkyunkwan University, Republic of Korea

8:00am **PS+SS+TF-WeM1 Atomic Layer Etching to Escape Process Tradeoffs for 7nm Technology and Beyond**, ***Alok Ranjan***, *M. Wang, S. Sherpa,* TEL Technology Center, America, LLC, *P. Ventzek*, Tokyo Electron America, Inc. **INVITED**

With shrinking critical dimensions, dry etch faces more and more challenges. Minimizing each of aspect ratio dependent etching (ARDE), bowing, undercut, selectivity, and within die uniformly across a wafer are met by trading off one requirement against another. The problem of trade-offs is especially critical for 10nm and beyond technology. At the root of the problem is that roles radical flux, ion flux and ion energy play may be both good and bad. Increasing one parameter helps meeting one requirement but hinders meeting the other. Self-limiting processes like atomic layer etching (ALE) promise a way to escape the problem of balancing trade-offs. ALE [1] was realized in the mid-1990s but the industrial implementation did not occur due to inherent slowness and precision loss from improper balance of self-limiting passivation and its removal processes. In recent years interest in ALE has revived and strides have been made by etch equipment manufacturers primarily through temporal, spatial or combination of these two pulsing approaches. Moderate success has been reported with some of the trade-offs purported to be managed. Difficulty meeting requirements is due to the inability of plasma technologies to control ion energy at low and precise values.

We overcome many of the practical implementation issues associated with ALE by precise passivation process control using plasmas with low electron temperature. Very low plasma potential, high radical flux and high bombardment flux are indispensable for achieving ALE. We demonstrate that ALE can achieve zero ARDE and infinite selectivity. Experimental results will highlight that careful consideration of surface process physics is required to achieve ALE and not simply "slow etching". Without profile control, ALE is not useful. Profile control will be shown to rely on careful management of the ion energies and angles. For ALE to be realized in production environment, tight control of IAD is a necessary. Experimental results are compared with simulation results generated using MCFPM [2] and theoretical scaling models to provide context to the work.

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8:40am **PS+SS+TF-WeM3 Understanding of new processes for Atomic Layer Etching**, ***Florentin Chambettaz,*** *L. Vallier, J. Dubois,* Univ. Grenoble Alpes-CNRS-CEA/Minatec-LTM,38000 Grenoble-France*, O. Joubert*, Univ. Grenoble Alpes-CNRS-CEA, France

In the pace of downscaling in microelectronic, current plasma etching processes show their limits. Actually for critical dimension smaller than 10 nm, atomic precision has to be reached during etching. In this study we are developing an Atomic Layer Etching (ALE) process by focusing on the induced damages related to the chemical and physical interaction(s) with hydrogen (This subject has already been broached in other studies on graphene [1] or carbon nanotubes [2]) and helium plasmas. Hydrogen plasmas have been used for years in the microelectronic industry and studied in the fields of deposition (PECVD, Plasma Enhanced Chemical Vapor Deposition), surface processing (surface passivation, hydrogenation) and plasma etching [3]. However the mechanisms related to these processes are not fully understood yet mainly because hydrogen is an element with peculiar characteristics such its low mass and its electronegativity. Helium plasmas have been also used for many years in the microelectronics industry. Helium is often employed in plasma processes as an additives gas due to its low chemical reactivity and low mass. Consequently ionic species present in the plasma and their effect are well known. To modify the surface of ultrathin layers without damaging the materials, a very low ion bombardment is required (conditions similar to those obtained in a pulsed ICP reactor [4]). At the same time, high energy plasmas are required to obtain satisfying etch rates when several nanometers have to be etched away. In this study we focus on plasma etching of silicon nitride by hydrogen plasma exposure in a commercially available 300 mm reactor, in order to develop an ALE process for spacer etching of future 10nm transistors. Several process conditions are achieved with different ion energies and ion densities, on thin silicon nitride blanket samples. The generated damages in the structure were quantified with an Electron Spin Resonance (ESR) spectroscopy and electrical characterization. The effect of these etching processes on silicon nitride will be discussed.

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9:00am **PS+SS+TF-WeM4 Self-Limited Ion Implantation for Precise Low-k Spacer Etching**, ***Nicolas Posseme***, Cea-Leti, Minatec, France*, M. Garcia-Barros, C. Arvet,* ST Microelectronics*, O. Pollet,* Cea-Leti, Minatec*, S. Lagrasta, P. Maury,* ST Microelectronics*, F. Leverd,* ST Microlectronics*, C. Richard,* ST Microelectronics*, S. Barnola*, Cea-Leti, Minatec, France

With aggressive device shrinking, parasitic capacitances through the spacer become a greater contributor to the total device capacitance. This issue is exacerbated by the common use of SiN spacers. Since SiN has a relatively large dielectric constant (k~7.5), a simple approach to reduce capacitive coupling through the spacer is to supplant it with a low-k material [1]. Therefore, the reduction of spacer k value is a key for the high performance devices. In this context, Low-k films like SiCO, SiOCN or SiBCN have been proposed for the C014 technology node to replace the traditional silicon nitride investigated.

Today, the Low-k spacer etching is considered as one of the most challenging step in the high performance FDSOI devices realization. A trade-off has to be found between silicon germanium (or silicon) recess, foot formation and CD control impacting the device performances. The etch process must also be compatible with epitaxial step.

In a recent study, we proposed a new etch approach [2] for silicon nitride spacer etching. This new etching process is based on a Self-Limited Ion Implantation by plasma. In a first step, the film is modified in volume by a Hydrogen plasma performed in a conventional etch tool (CCP or ICP) followed in a second step by a 1%HF wet cleaning to remove the modified layer selectively to the non-modified material. We demonstrated that the silicon germanium recess was estimated to less than 6A with no foot formation, while a silicon germanium has grown by epitaxy without defects [2].

In this study, we propose to evaluate the compatibility of this new etch approach with low-k films like SiCO or SiCBN. By playing on plasma operating conditions performed in ICP etch tool, we will demonstrate that the Low-k films can accurately be etched with atomic layer control, stopping on SiGe or Si. The key parameters for such etch precision are identified as H ion energy and H ion dose implanted in the low-k film. The etch mechanisms to remove the modified layer by wet cleaning process will be understood on blanket wafers thanks to XPS and infrared spectroscopy analyses.

Finally the compatibility of this new Low-k spacer etching process with the epitaxial step will also be presented for C014 FDSOI integration.

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9:20am PS+SS+TF-WeM5 Self-limiting Cyclic Etching of Silicon Nitride using Infrared Irradiation

Nobuya Miyoshi, Hitachi, Japan, *H. Kobayashi, K. Shinoda,* Hitachi*, M. Matsui,* Hitachi, Japan*, M. Miyake, K. Maeda,* Hitachi*, Y. Kouzuma,* Hitachi High-Technologies, Japan*, Y. Kudo, T. Kanekiyo, M. Izawa*, Hitachi High-Technologies

Advanced semiconductor device fabrication requires precise control of device dimensions down to the atomic level. Current efforts to achieve atomic level control are focused on cyclic etching that repeatedly forms and removes a reactive layer on a surface. The cyclic etching of SiO_2, for example, has been achieved by repeatedly forming and removing of ammonium hexafluorosilicate ($(NH_4)_2SiF_6$) [1]. The essential point in realizing atomic level control is achieving a self-limiting process.

Fluorocarbon-based plasma produces a $(NH_4)_2SiF_6$ layer on silicon nitride surfaces [2]. We have reported the preliminary results of the cyclic etching of silicon nitride using the formation and removal of the $(NH_4)_2SiF_6$ layer [3]. An analysis using x-ray photoelectron spectroscopy (XPS) revealed that the $(NH_4)_2SiF_6$ layer formed on silicon nitride after exposure to fluorocarbon-based plasma and was desorbed by annealing the sample.

In this study, the removal of the $(NH_4)_2SiF_6$ layer using IR irradiation was investigated to achieve high-throughput cyclic etching. The reactive layer of $(NH_4)_2SiF_6$ was formed on a silicon nitride sample after exposure to radicals in fluorocarbon-based plasma. After formation of the reactive layer, IR light was irradiated to the sample for removal. The sample surface was analyzed by XPS, and the dependence of the etching depth on the radical exposure time was investigated. The temperature of the sample increased over 160°C under IR irradiation for 10 s. A nitrogen 1s peak at 402 Ev, which is attributed to $(NH_4)_2SiF_6$, disappeared after IR irradiation for 10 s. This result shows that IR irradiation is expected to result in fast removal of the reactive layer within 10 s. The etching depth after IR irradiation saturated at 1 nm as the radical exposure time was increased to over 300 s. Therefore, a self-limiting process for silicon nitride was obtained by forming and removing the $(NH_4)_2SiF_6$ layer. Finally, the cyclic etching was investigated by repeatedly forming and removing the reactive layer. The number of cycles was changed between 1 and 10. The total etching depth increased linearly with the number of cycles, demonstrating the cyclic etching of silicon nitride with high precision.

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9:40am PS+SS+TF-WeM6 Prospects for Thermal Atomic Layer Etching: Materials and Selectivity

Steven George, *Y. Lee, J.W. DuMont*, University of Colorado at Boulder

Thermal atomic layer etching (ALE) of Al_2O_3 and HfO_2 has recently been demonstrated using sequential, self-limiting reactions [1-3]. Al_2O_3 and HfO_2 ALE were performed using $Sn(acac)_2$ and HF as the reactants [1-3]. Recent work has also shown that Al_2O_3 ALE can be accomplished using $Al(CH_3)_3$ and HF as the reactants. The ALE reaction mechanism is believed to involve fluorination and ligand-exchange. For Al_2O_3 ALE using $Sn(acac)_2$ and HF, HF exposures convert Al_2O_3 to AlF_3. $Sn(acac)_2$ then accepts F from AlF_3 and donates acac to AlF_3 to produce volatile $Al(acac)_3$ or $AlF(acac)_2$.

The prospects for thermal ALE are very promising. Thermochemical calculations suggest that many materials should be etched with similar reactions. Metal oxides, metal nitrides, metal phosphides, metal arsenides and elemental metals can all be fluorinated with fluorine reactants such as HF or XeF_2 to form the corresponding metal fluoride. Ligand-exchange reactions can then be conducted with a variety of metal precursors that accept fluorine from the metal fluoride and donate one of their ligands to the metal in the metal fluoride. The metal reaction products then can leave the surface if they are stable and volatile. Preliminary results for GaN etching suggest that metal nitrides are good candidates for thermal ALE.

The metal fluoride reaction products produced by the ligand-exchange process provide pathways for selectivity during thermal ALE. Selectivity can arise depending on the stability of the metal reaction product. For example, $Sn(acac)_2$ is a metal beta-diketonate that donates acac ligands to the metal in the metal fluoride. Because most metals bind with acac ligands, $Sn(acac)_2$ may not lead to significant selectivity. In contrast, $Al(CH_3)_3$ is a metal alkyl that donates CH_3 ligands to the metal in the metal fluoride. Because some metals do not easily form sigma-bonds to bond to CH_3 ligands, more complete selectivity between different materials may be expected for $Al(CH_3)_3$. The selectivity observed between Al_2O_3 and ZrO_2 etching will illustrate this concept.

1. Younghee Lee and Steven M. George, "Atomic Layer Etching of Al_2O_3 Using Sequential, Self-Limiting Thermal Reactions with $Sn(acac)_2$ and HF", *ACS Nano* **9,** 2061 (2015).

2. Younghee Lee, Jaime W. DuMont and Steven M. George, "Mechanism of Thermal Al_2O_3 Atomic Layer Etching Using Sequential Reactions with $Sn(acac)_2$ and HF" *Chem. Mater*. (In Press).

3. Younghee Lee, Jaime W. DuMont and Steven M. George, "Atomic Layer Etching of HfO_2 Using Sequential, Self-Limiting Thermal Reactions with $Sn(acac)_2$ and HF", *J. Solid State Sci. Technol*. **4**, N5013 (2015).

11:00am PS+SS+TF-WeM10 Atomic Layer Etching of Al_2O_3 Using Sequential, Self-Limiting Thermal Reactions with Trimethylaluminum and Hydrogen Fluoride

Younghee Lee, *J.W. DuMont, S.M. George*, University of Colorado, Boulder

A new approach for the atomic layer etching (ALE) of Al_2O_3 was demonstrated using sequential, self-limiting thermal reactions with trimethylaluminum (TMA) and hydrogen fluoride (HF) as the reactants. Previously, Al_2O_3 thermal ALE was reported using $Sn(acac)_2$ and HF as the reactants [1,2]. HfO_2 ALE was also demonstrated using $Sn(acac)_2$ and HF as the reactants [3]. This new approach using TMA expands the variety of ALE reactants and excludes the possibility that Sn could be left on the etched Al_2O_3 film.

Quartz crystal microbalance (QCM) experiments monitored Al_2O_3 ALE at temperatures from 275-325°C. The Al_2O_3 ALE was linear versus number of TMA and HF reaction cycles. The QCM studies showed that the sequential TMA and HF reactions were self-limiting versus reactant exposure. The QCM analysis measured a mass change per cycle (MCPC) of -16 ng/(cm^2 cycle) at 300°C. This MCPC corresponds to an Al_2O_3 etch rate of 0.53 Å/cycle. X-ray reflectivity analysis confirmed the linear removal of Al_2O_3 and etching rates. Fourier transform infrared spectroscopy measurements also monitored Al_2O_3 ALE by observing the loss of infrared absorbance from Al-O stretching vibrations.

Al_2O_3 ALE is believed to follow the reaction: $Al_2O_3 + 4Al(CH_3)_3 + 6HF \rightarrow 6AlF(CH_3)_2 + 3H_2O$. The proposed reaction mechanism involves fluorination and ligand-exchange. The HF exposure fluorinates Al_2O_3 and forms AlF_3 with H_2O as a reaction product. During ligand-exchange, $Al(CH_3)_3$ accepts F from AlF_3 and donates CH_3 to AlF_3 to produce volatile $AlF(CH_3)_2$ reaction products. Similar reaction mechanisms based on fluorination and ligand-exchange reactions may extend the range of thermal ALE to a wide variety of additional materials.

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2. Younghee Lee, Jaime W. DuMont and Steven M. George, "Mechanism of Thermal Al_2O_3 Atomic Layer Etching Using Sequential Reactions with $Sn(acac)_2$ and HF" *Chem. Mater*. (In Press).

3. Younghee Lee, Jaime W. DuMont and Steven M. George, "Atomic Layer Etching of HfO_2 Using Sequential, Self-Limiting Thermal Reactions with $Sn(acac)_2$ and HF", *J. Solid State Sci. Technol*. **4**, N5013 (2015).

11:20am **PS+SS+TF-WeM11 Low Damage Etch Chamber for Atomic Layer Etching**, ***Leonid Dorf***, *S.R. Dorf, T.G. Monroy, K. Ramaswamy, K.S. Collins, Y. Zhang*, Applied Materials

The use of novel, ultra-sensitive materials requires low-damage plasma etching with atomic layer precision, which imposes progressively stringent demands on accurate control over ion energy and radical composition during plasma processing. Using electron sheet beam (e-beam) parallel to the substrate surface to produce plasma in a processing chamber provides an order of magnitude reduction in electron temperature T_e (~ 0.3 eV) and ion energy E_i (< 2 eV without applied bias) compared to conventional plasma technologies, thus making electron beam plasmas an ideal candidate for processing features at 5 nm and below. Furthermore, since dissociation is performed only by high-energy beam and not plasma electrons, and the dissociation cross-section drops off considerably at beam energies of about 1–2 keV, the beam created plasma is typically poor in radicals, which allows an independent control over plasma radical composition. In this presentation, we describe the Low Damage Etch Chamber (LoDEC) for atomic layer etching (ALE). The apparatus consists of (1) an e-beam source for creating radical-poor, low-T_e plasma in the processing chamber, (2) a remote plasma source (RPS) for producing and supplying radicals to the substrate, and (3) a bias generator for creating the voltage drop (with fine control in 0 – 50 V range) between the substrate and the plasma to accelerate ions over etch-threshold energies. Using patterned wafers, we have developed low-bias power (0 – 10 W) processes resulting in very high selectivity (as per high-resolution TEM images) of Si_3N_4 to SiO_2 and poly-Si in fluorocarbon based chemistries. In application to ALE, we note that one existing approach to ALE of Si prescribes injecting Cl atoms to passivate the surface, and then replacing the processing gas with Ar and applying bias to the substrate to initiate the etching. Once the passivation layer is removed, the etch stops, provided Ar^+ ions have energies below sputtering threshold. By repeating passivation and etching steps, this scheme can be used to remove silicon in equally thick portions composed of one to a few atomic layers (few Amgstroms), without tight control over the duration of the bias part of the cycle. In LoDEC, this recent pulsed-ALE technique can be performed at ion energies much lower than that in conventional tools, thus minimizing damage to the processed materials. LoDEC also allows implementation of a unique, truly low damage, continuous-ALE technique by using electron beam to create plasma with very low ion energies (with or without an application of low-power bias to accelerate ions) and RPS to create radicals. The results of ALE experiments in LoDEC will be presented.

11:40am **PS+SS+TF-WeM12 Modeling of Electron-Beam Generated Plasmas: Validation and System Design**, ***Shahid Rauf***, *A. Agarwal, L. Dorf, K.S. Collins,* Applied Materials, Inc., *D.R. Boris, S.G. Walton*, US Naval Research Laboratory

Plasmas generated using energetic electron beams have unique properties that make them attractive for emerging plasma processing applications. In the work done at the Naval Research Laboratory, [1] it has been demonstrated that electron temperature (T_e) in the electron-beam plasmas generated in molecular gases is typically < 0.6 eV while electron densities are comparable to those obtained in radio-frequency (RF) inductively and capacitively coupled plasmas. In addition, the ions and radicals are primarily produced by highly energetic electrons (few keV) instead of electrons in the tail of a low energy distribution. The plasma chemistry in electron-beam generated plasmas is therefore significantly different than RF plasmas with a much higher ion to neutral radical density ratio in electron beam plasmas. As feature dimensions shrink below 20 nm in microelectronics devices with atomic level precision required during manufacturing, the unique properties of electron-beam generated plasmas (low T_e, low ion energy and unique chemistry) are becoming attractive for plasma processing in the semiconductor industry.

This paper focuses on a multi-dimensional computational model for electron-beam generated plasmas. A fluid model for the bulk plasma is coupled with a Monte Carlo kinetic model for beam electrons. The fluid plasma model uses the drift-diffusion approximation for electrons and negative ions. The momentum equation is solved for positive ions. The model includes the effect of magnetic field on charged species transport. The Monte Carlo model for beam electrons considers electron motion in the ambipolar electric field and externally imposed static magnetic field. Additionally, important collision processes including elastic collisions, ionization, excitation, dissociation and dissociative attachment are considered during the Monte Carlo simulation.

The computational model is validated in Ar, Ar/N_2 and O_2 plasmas using probe measurements over a range of gas pressures and electron beam properties. One factor that has important implications on quantitative accuracy of the model is the influence of magnetic field on electron transport properties. The paper will discuss the classical transport model as well as variations based on semi-empirical approximations. The validated model is applied to the design of electron beam based plasma processing systems.

This work was partially supported by the Naval Research Laboratory Base Program.

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12:00pm **PS+SS+TF-WeM13 Enhanced Reaction Rate and Precursor Transport in Focused Electron Beam Induced Etching Via Pulsed Laser Assistance**, ***JooHyon Noh***, University of Tennessee, *J.D. Fowlkes,* Oak Ridge National Laboratory, *R. Timilsina, M.G. Stanford, B.B. Lewis, P.D. Rack*, University of Tennessee

Focused electron-beam-induced etching (FEBIE) is a versatile, selective or direct write nanomaterials etching technique, and is an alternative to focused ion beam (FIB) etching. FIB etching can cause collateral sub-surface damage due to knock-on collisions and ion implantation. FEBIE in contrast is minimally invasive because of the low electron mass and offers high etch selectivity between different materials. Additionally, the FEBIE process has better spatial resolution due to the smaller beam spot size. However, the low FEBIE etch rate has been a limiting factor for high-throughput applications.

The FEBIE process is governed by an electron-induced reaction with a precursor at the substrate surface, resulting in the volatile etch by-products. This complex process can be rate limited by different mechanisms depending on the electron and precursor parameters, the electron stimulated reaction rates, and the by-product volatility (or residence time). While substrate heating can reduce the by-product residence time, the higher temperature concomitantly decreases the reactant residence time, which can reduce the reactant equilibrium coverage and result in the electron stimulated etching rate. In order to enhance the etch rate, we introduce a laser-assisted focused electron-beam-induced etching (LA-FEBIE) process which emulates an atomic layer etching process. The focused electron beam catalyzes the first half reaction which forms a pseudo-volatile byproduct. The periodic and appropriately synchronized pulsed laser can locally and briefly raise the surface temperature, which can affect the reactant and byproducts and facilitate the reaction kinetics. In this presentation we will overview the laser-assisted electron beam induced etching of Ti with a XeF_2 gas chemistry and will correlate the mechanisms to a selected area atomic layer etching process. We will show results that the Ti electron stimulated etch rate via the XeF_2 precursor can be enhanced up to 6 times with an intermittent pulsed laser assist. The etching evolution is correlated to in situ stage current measurements and scanning electron micrographs as a function of time. Other relevant work on conventional fluorine-based titanium plasma etching suggests the mechanism of Ti-F etching is attributed to the reaction of F radicals with Ti to form TiF_x products; where progressive fluorine incorporation drives x towards the volatile product of TiF_4. Notably TiF_3 is a stable solid at room temperature. The increased etch rate with laser assistance is attributed to photothermally enhanced Ti−F reaction and TiF_4 desorption and in some regimes enhanced XeF_2 surface diffusion to the reaction zone.

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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[2] M. Polini, F. Guinea, M. Lewenstein, H. C. Manoharan, V. Pellegrini, "Artificial Honeycomb Lattices for Electrons, Atoms, and Photons," *Nature Nanotechnology* **8**, 625–633 (2013).

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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3. D. Asakura *et al.* Phys. Rev. Lett. 93, 247006 (2004).
4. N. Delbosc et al. RSC Adv 4, 15236 (2014).

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 MoS_2**, ***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)$\sqrt{3}$x$\sqrt{3}$-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)$\sqrt{3} \times \sqrt{3}$-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))$\sqrt{3} \times \sqrt{3}$-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 $\sqrt{3} \times \sqrt{3}$ 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))$\sqrt{3} \times \sqrt{3}$-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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[2] G. Bian, X. Wang, T. Miller, T. -C. Chiang, P. J. Kowalczyk, O. Mahapatra, S. A. Brown, Phys. Rev. B 90, 195409 (2014).

[3] I. Kokubo, Y. Yoshiike, K. Nakatsuji, H. Hirayama, Phys. Rev. B 91, 075429 (2015).

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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 ($\sqrt{3}$ x $\sqrt{3}$)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 $\sqrt{3}$-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/O_2 and H_2O Plasma Modified SnO_2 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 CO_2 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.

Surface Science
Room: 112 - Session SS-WeM

Environmental Interfaces, Ambient Surfaces, In-Operando Studies and Adsorption on 2D Materials
Moderator: Peter Sutter, University of Nebraska - Lincoln

8:00am **SS-WeM1 Liquid-Jet Ambient Pressure Photoelectron Spectroscopy Studies of the Liquid/Vapor Interface of 1-Propanol and 2-Propanol Aqueous Solutions**, ***Michael Makowski***, *J.M. Langford, D. Tobias, J.C. Hemminger*, University of California Irvine

The liquid/vapor interface of aqueous 1- and 2-propanol solutions for a broad range of concentrations was studied using a liquid-jet ambient pressure X-ray Photoelectron Spectroscopy system at the Advanced Light Source synchrotron in the Lawrence Berkeley National Laboratory. At low concentrations, 1-propanol displays a clear propensity to lie at the solution surface, evidenced by an enhanced carbon 1s XPS signal for electrons of low kinetic energy. Near a concentration (mole fraction) of 0.01 mf, a surface layer of 1-propanol appears to saturate, as evidenced by the saturation of the carbon 1s to oxygen 1s XPS signal ratio. Furthermore, over increasing concentrations carbon and oxygen 1s binding energies show a sharp redshift of 1 eV, until reaching a concentration of approximately 0.01 mf. This suggests an increasing 1-propanol density at the surface, with the resulting surface dipole layer causing a shift in the observed C1s and O1s binding energies for the condensed species.

These results of aqueous 1-propanol are compared and contrasted to similarly obtained aqueous 2-propanol carbon and oxygen spectra. Moreover, experimental results were corroborated with classical molecular dynamics simulations. Density profiles relative to an instantaneous interface were calculated for aqueous 1-propanol solutions. MD simulations indicate that 1-propanol accumulates at the surface at very low concentrations an a surface layer saturates at approximately 0.01 mf in agreement with the experimental results.

8:20am **SS-WeM2 Near Ambient Pressure XPS at the SLS – *In Situ* Cell Design for Solid/Vapor Interfaces and First Results in Environmental TiO_2 Photocatalysis**, ***Fabrizio Orlando***, Paul Scherrer Institut, Switzerland, *A. Waldner*, Paul Scherrer Institut and ETH Zürich, Switzerland, *M.-T. Lee*, Paul Scherrer Institut and University of Bern, Switzerland, *M. Birrer, T. Bartels-Rausch*, Paul Scherrer Institut, Switzerland, *C. Proff*, Paul Scherrer Institut and ETH Zürich, Switzerland, *T. Huthwelker, A. Kleibert*, Paul Scherrer Institut, Switzerland, *J. van Bokhoven*, Paul Scherrer Institut and ETH Zürich, Switzerland, *M. Ammann*, Paul Scherrer Institut, Switzerland

Near ambient pressure X-ray photoelectron spectroscopy (NAPP) is a powerful tool to investigate elemental composition and chemical specificity of surfaces under reaction conditions that offers tremendous opportunities in environmental science and heterogeneous catalysis research. In the first part of this contribution I will provide a brief outlook on a new analysis chamber for the NAPP endstation at the Swiss Light Source that is designed for in situ XPS and NEXAFS at solid/vapor interfaces under environmentally relevant conditions of temperature and pressure (up to 20 mbar and 100% relative humidity) [1]. The flow-tube design of this new chamber allows to perform in situ measurements at high pressure and UHV conditions one after the other in the same analysis cell, while at the same time reducing the exposed volume and surface area of the analysis cell. Moreover, this chamber features (i) a direct access from a gas dosing system down to the sample, allowing for the admission of sticky gases with reduced wall effects, and (ii) a UV laser setup, providing the opportunity to investigate photoactive materials under atmospherically relevant conditions of pressure and light with reduced extent of gas phase photochemistry induced by the UV-light. We have used this novel chamber to investigate photocatalysis on TiO_2, which is a component of natural mineral dust that represents an important reactive aerosol in the atmosphere affecting the ozone budget and the climate. In this context, adsorption of water and hydroxylation of the surface, which are key aspects to understand TiO_2 photocatalysis in the environment, offer still major open questions. Earlier NAPP studies have provided important insight into the nucleation of water on this surface [2]. In a recent study we have quantified the effect of humidity on ozone-induced band bending on the TiO_2(110) surface [3], and found interesting changes in XPS and NEXAFS spectra indicative of changes in the hydrogen bonding structure in multilayers of water [4]. I will discuss our most recent NAPP investigation on the influence of UV light and humidity on the adsorption of water on a TiO_2 powder sample surface. Our results indicate an enhancement of water adsorption under UV irradiation, which might be the basis to explain light-induced superhydrophilicity previously observed on TiO_2-based nanomaterials. I will also briefly illustrate an application study on the uptake of trace gases on ice surface.

References

[1] F. Orlando et al., submitted.

[2] G. Ketteler et al., J. Phys. Chem C 111, 8278 (2007).

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[4] M. Lampimäki et al., J. Phys. Chem. C 119, 7076 (2015).

8:40am **SS-WeM3 Ambient Pressure XPS Observation of Electrode Surfaces During Electrochemical Reactions**, ***Hirohito Ogasawara***, *S. Kaya, H.S. Sanchez Casalongue, M.L. Ng, D. Friebel, A. Nilsson*, SLAC National Accelerator Laboratory

We have been focusing on identifying the surface electronic structure and chemical nature of catalytic electrodes during electrochemical reactions through the use of synchrotron-based ambient pressure photoemission spectroscopy (APXPS) [1]. One of the crucial factors that limit electrochemical water splitting is the large overpotential required for the oxygen evolution reaction. Iridium oxide, which is one of the most widely used anode catalyst, has been shown to have high activity and stability in water electrolysis. APXPS studies indicate both oxide and hydroxide species on the catalyst surface. Under electrochemical oxygen evolution conditions, iridium undergoes a change in oxidation state, which takes place predominantly at the surface of the catalyst [2]. Molybdenum sulfides are promising materials in the search for cost-effective cathode catalyst. We tracked the transformation of amorphous MoS_3 nanoparticles during electrochemical hydrogen evolution reactions. We observed that surface sites are converted from MoS_3 to MoS_2 increasing MoS_2 edge-like sites with high activity [3]. The sluggish kinetics in oxygen reduction reaction is one of the key challenges in polymer electrolyte membrane fuel cells. We established that the species on the platinum catalytic electrode change drastically depending on the oxygen pressures. We used this knowledge to clarify that the reaction pathway is dependent on the operating conditions [4].

References

[1] S. Kaya, H. Ogasawara, L.-Å. Näslund, J.-O. Forsell, H. Sanchez Casalongue, D.J. Miller, A. Nilsson, *Catalysis Today*205 (2013) 101

[2] H. Sanchez Casalongue, M.L. Ng, S. Kaya, D. Friebel, H. Ogasawara, A. Nilsson, *Angewandte Chemie* **126** (2014) 7297

[3] H. Sanchez Casalongue, J.D. Benck, C. Tsai, R.K.B. Karlsson, S. Kaya, M.L. Ng, L.G.M. Pettersson, F. Abild-Pedersen, J.K. Nørskov, H. Ogasawara, T.F. Jaramillo, A. Nilsson, *J. Phys. Chem. C* **118** (2014) 29252

[4] H. Sanchez Casalongue, S. Kaya, V. Viswanathan, D.J. Miller, D. Friebel, H.A. Hansen, J.K. Nørskov, A. Nilsson, H. Ogasawara, *Nature Communications* **4** (2013) 2817

9:00am **SS-WeM4 Formation of Heterogeneous Multiple-Oxide/Hydroxide Species on a GaP(111) Surface Tracked by *In Situ* Near-Ambient Pressure XPS**, ***Xueqiang Zhang***, *S. Ptasinska*, University of Notre Dame

A photoelectrochemical (PEC) solar cell for water splitting converts solar energy into chemical energy and store it in the form of hydrogen, which is a promising candidate of sustainable and clean fuels. PEC solar cells consisted of phosphide-based III-V semiconductors are known to have a higher solar to hydrogen conversion efficiency than other materials. They are, however, usually limited by technological drawbacks such as photocorrosion or decreased electron extraction efficiency due to the formation of surface oxide species. The formation of surface oxides becomes critical when operating electrodes are exposed to aqueous electrolytes or to ambient conditions. Therefore, it is desirable to understand the interfacial processes of water interactions with semiconductors, and to elucidate possible oxidation and reduction mechanisms at the H_2O/semiconductor interface, especially under near realistic conditions.

In this study, water dissociative adsorption onto a GaP (111) surface was investigated using near ambient pressure X-ray photoelectron spectroscopy (NAP XPS) at various pressures and temperatures [1]. This advanced technique allowed us to monitor the H_2O/semiconductor interfacial chemistry under *operando* conditions, which would not be feasible to be investigated by traditional surface sensitive techniques. The interfacial chemistry was tracked by recording high-resolution photoemission spectra of Ga $2p_{3/2}$, O 1s, and P 2p. In the pressure-dependent study conducted at room temperature, ~300 K, the enhancement of surface Ga hydroxylation and oxidation was observed with an increase in H_2O pressures. This finding was also confirmed by changes observed in the photoemission spectra of O 1s. In the temperature dependent study, surface Ga hydroxylation and oxidation were further enhanced at temperatures below 673 K. While a large-scale conversion of surface O-Ga-OH species into Ga hydroxide, along with surface P oxidation, were observed at 773 K. Moreover, the formation of Ga and P oxide/hydroxide networks was suggested and a "phase diagram" that demonstrates the distribution of different chemical species under various experimental conditions has been generated (supplemental document). Our results led to a better understanding of the H_2O/semiconductor interfacial chemistry and the water splitting mechanism in the PEC solar cells.

Reference

1. Zhang, X., Ptasinska, S. Distinct and dramatic water dissociation on GaP(111) tracked by near-ambient pressure X-ray photoelectron spectroscopy. Phys. Chem. Chem. Phys., 2015, 17, 3909-3918.

9:20am **SS-WeM5 Investigation of Liquid/Solid Interfaces using Photoelectron Spectroscopy**, ***Hendrik Bluhm***, Lawrence Berkeley Lab, University of California, Berkeley **INVITED**

Solid/vapor, liquid/vapor and liquid/solid interfaces govern many processes in the environment, heterogeneous catalysis, and technology. Ambient pressure photoelectron spectroscopy is an excellent method for the characterization of these interfaces under operating conditions, in particular since it affords to correlate the elemental and chemical composition at the interface with the electrical potentials. This talk will focus on the application of APXPS to the investigation of liquid/solid surfaces under realistic conditions, which is arguably the next frontier in surface science. We will highlight the application of ambient pressure XPS in combination with standing waves for the investigation of the electric double layer at solid liquid interfaces in environmental science and corrosion chemistry.

11:00am **SS-WeM10 Surface and Bulk Crystallization Kinetics of Amorphous Solid Water Nanoscale Films**, ***R. Scott Smith***, *C. Yuan, R.A. May, B.D. Kay*, Pacific Northwest National Laboratory

We investigate the crystallization kinetics of nanoscale amorphous solid water (ASW) films using temperature-programmed desorption (TPD) and reflection absorption infrared spectroscopy (RAIRS). ASW is a metastable form of water created by vapor deposition on a cold substrate ($T < 130$ K). In prior work, we reported the episodic release of trapped gases in concert with the crystallization of ASW, a phenomenon that we termed the "molecular volcano." The observed abrupt desorption is due to the formation of cracks that span the film to form a connected pathway for release. In a recent study we used the selective placement of an inert gas layer is used to show that cracks form near the top of the film and propagate downward into the film. Those experiments showed that, after some induction time, cracks propagate linearly in time with an Arrhenius dependent velocity consistent with the crystallization growth rates reported by others. This suggested a direct connection between the crystallization growth and the crack propagation rate. In the present study we directly measure the surface (using TPD) and bulk (using RAIRS) ASW crystallization kinetics as a function of film thickness. These results show that nucleation and crystallization begins at the ASW/vacuum interface and then the crystallization growth front propagates linearly into the bulk. The details of the experiment and the interpretation of the results will be discussed in detail.

This work was supported by the US Department of Energy, Office of Science (DOE), Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences & Biosciences. The research was performed using EMSL, a national scientific user facility sponsored by DOE's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory, which is operated by Battelle operated for the DOE.

11:20am **SS-WeM11 Environmental Effects on Oxidative Surface Passivation Across $Al_xFe_yNi_{1-x-y}$ Composition Space**, ***Matthew Payne***, *J.B. Miller, A.J. Gellman*, Carnegie Mellon University

Alloys that derive robust oxidation resistance by the preferential formation of a passivating Al_2O_3 scale are commonly used for structural applications in thermochemically harsh operating environments. Often, one of the primary design concerns is to determine the lowest Al content required to induce passivation, so as to minimally impair the mechanical properties of the material. This "critical Al concentration" is kinetically dictated and can depend strongly on both multicomponent composition and the nature of the oxidizing environment. We have previously developed high-throughput methodology to study oxidation using composition spread alloy films (CSAFs), combinatorial sample platforms with continuous lateral composition gradients. Behavior related to oxidative corrosion and passivation can be characterized continuously across an entire ternary composition space with a single CSAF, using a combination of spatially resolved techniques including optical imaging, scanning electron microscopy, energy-dispersive X-ray spectroscopy, Raman spectroscopy, and X-ray photoemission depth profiling. We have used this methodology to compare the oxidation of $Al_xFe_yNi_{1-x-y}$ alloys at 700 K in dry-air and humid-air environments. The critical Al concentration in the Fe-rich region of composition space was found to be significantly higher for exposure to the humid air. The continuous nature of the results provides valuable fundamental insight into the interplay of composition and environment on alloy oxidation kinetics.

11:40am **SS-WeM12 Hydrogen-Bonded Self-Assembled Molecular Structures on Hexagonal Boron Nitride**, ***Vladimir Korolkov***, *S. Svatek, L. Yang, J. Kerfoot, A. Summerfield, N. Champness,* University of Nottingham, UK, *T. Taniguchi, K. Watanabe,* The National Institute for Materials Science, Japan, *N. Besley, P. Beton*, University of Nottingham, UK

Hexagonal boron nitride (h-BN) is a layered material and a wide-gap semiconductor with a band gap of 5.2 e.V. The latter property makes it highly attractive as a support to study optical and electrical properties of monolayered molecular assemblies stabilized by non-covalent interactions. Although h-BN has been known since 1940s it is a relatively new substrate in the area of molecular self-assembly. In part this is due to the widespread use of scanning tunneling microscopy to acquire images of molecules, but this technique is not compatible with h-BN.

The adsorption of a range of molecules on BN and other layered materials has been investigated using using high resolution atomic force microscopy (AFM). We have observed several arrangements of molecules which are stabilized by hydrogen bonding including a bimolecular layer formed by perylene tetracarboxylic di-imide (PTCDI) and melamine which form an open nanporous array in which the planar PTCDI molecules are adsorbed parallel to the substrate. The networks are deposited from solution by immersion of BN substrate and the ordering may be improved by post-annealing in an inert atmosphere. We have also investigated the adsorption of 5,10,15,20-tetrakis(4- carboxylphenyl)porphyrin (TCPP), a dye molecule with a planar porphyrin macrocycle as its core. This molecule forms an open square array, also stabilized by hydrogen bonding through carboxlic acid pendant groups which steer the arrangement so that macrocycle lies parallel to the surface. In this arrangement the molecular layer is strongly fluorescent showing lines which are red-shifted from solution. When molecules are adsorbed on MoS2 they form similar structures but the resulting islands are smaller and less ordered, and, due to the smaller band gap of MoS2, fluorescence is quenched. We also present density functional theory calculations of the conformation of adsorbed molecules and numerical estimates of the hydrogen bonding and adsorption energies. We discuss this approach as a route to the molecular functionalization of two-dimensional materials and the formation of hybrid molecular devices.

The work will present an outstanding examples of single molecule and submolecular resolution achieved in the ambient on standard Atomic Force Microscopes. Most of the presented results will be on level with the published UHV-STM studies.

12:00pm **SS-WeM13 Suppression of the Topological Surface State of Bi_2Te_3 by the Organic Molecule Manganese Phthalocyanine**, ***Andrew Hewitt***, *J. Boltersdorf, P.A. Maggard, D.B. Dougherty*, North Carolina State University

Organic molecules coupled to the spin-textured topological surface states of a topological insulator (TI) are expected to result in an interface ideal for organic spintronic devices.[1] Exploiting interfacial control at molecule-functionalized TI surface is a crucial step in realizing the potential of these new materials. It has been shown[2] that such a coupling may exist, along with a new hybrid-interface state above the Fermi level, between the magnetic molecule Manganese Phthalocyanine (MnPc) and the TI Bi_2Te_3. We report the suppression of the topological surface state by the adsorption of MnPc molecules as measured by Ultraviolet Photoelectron Spectroscopy. We show a new state emerging below the Fermi level at less than a monolayer coverage of MnPc molecules. The new interface state is different than the topological surface state and the molecular orbitals of the MnPc molecules as evidenced by the modified dispersion with Angle-Resolved Photoelectron Spectroscopy. We also observe an *n*-doping effect as charge is transferred from the molecule to the TI substrate in agreement with recent work.[2,3] We suggest that this interface system may have important implications for understanding the role of local time reversal symmetry breaking in TI's and in controlling spin injection into these novel materials.

[1] Jakobs *et al.* DOI: 10.1021/acs.nanolett.5b02213

[2] Sessi *et al.* Nano Lett. 2014, 14, 5092−5096

[3] Bathon *et al.* Nano Lett. 2015, 15, 2442−2447

Thin Film
Room: 111 - Session TF+EN-WeM

ALD for Energy
Moderator: Jesse Jur, North Carolina State University, Angel Yanguas-Gil, Argonne National Lab

8:00am **TF+EN-WeM1 Photovoltage Design for ALD Metal Oxide Protected Solar-Water-Splitting Photoanodes**, ***Andrew Scheuermann***, *J.P. Lawrence, K.W. Kemp, O.L. Hendricks,* Stanford University, *A. Walsh, I. Povey, M.E. Pemble, P.K. Hurley,* Tyndall National Institute, *C.E.D. Chidsey, P.C. McIntyre*, Stanford University

Metal oxide protection layers for photoanodes may enable the development of large-scale solar fuel and chemical synthesis. ALD-TiO_2 is the most widely used material because of its excellent stability under water oxidation conditions and potential for high electrical conductivity both as an ultrathin film and with thicknesses exceeding 100 nm [1-3]. However, the most conductive ALD-TiO_2 films exhibit poor photovoltages of ~ 400 mV and less [3]. Even assuming near-ideal fill factors, these voltages fall far short of the values needed for viable water splitting devices. Photovoltage optimization is especially difficult to achieve in MOS photoanodes because of the presence of a defective metal oxide protection layer and a defective semiconductor/oxide interface in the device structure. Therefore, understanding how to optimize photovoltage and stability is of utmost concern for the advancement of the field.

Here we report a novel observation of photovoltage loss associated with charge transfer in these metal-oxide protected devices, and by eliminating it, achieve photovoltages as high as 630 mV, the maximum reported to date for single-junction water-splitting silicon cells. The loss mechanism is systematically probed in MOS Schottky junction cells compared to buried junction p^+n cells, revealing the need to maintain a characteristic hole density at the semiconductor/insulator interface. A capacitor model that predicts this loss is developed, and is related to the dielectric properties of the protective oxide, achieving excellent agreement with the data. From these findings, we extract design principles for simultaneous optimization of charge transfer resistance and interface quality to maximize the photovoltage of metal-oxide protected MOS water splitting devices.

[1] Y.W. Chen, et al. *Nature Mat.* 2011, **10**, 539-544.

[2] A. G. Scheuermann, et al. Energy Environ. Sci. 2013, **6**, 2487–2496.

[3] S. Hu, et al. Science 2014, **344**, 1005−1009.

Supplemental Figure 1 | Charge transfer in three cell types for water splitting applied to silicon: Shows the Type 0 Semiconductor-Liquid (SL), Type 1 Metal-Insulator-Semicondcutor (MIS), and Type 2 p^+n junction. The density of states on either side of the oxides and the exciton splitting position with respect to these layers play a crucial role in mediating efficient charge transfer. These effects are so strong that Type 0 protected silicon cells exhibit essentially no photovoltage, Type 1 nSi cells show a linear photovoltage loss with oxide thickness, and Type 2 cells--where the hole concentration on the Si/SiO_2 interface is always high--exhibit record photovoltages at all oxide thicknesses and pH values studied.

8:20am **TF+EN-WeM2 Activity and Thermal Stability Enhanced Platinum catalysts with Nano-scale Oxide Coating via Atomic Layer Deposition**, ***Kun Cao***, *J.M. Cai, B. Shan, R. Chen*, Huazhong University of Science and Technology, Wuhan, China

Platinum nanoparticles (NPs) play an important role in the catalytic applications such as conversion of automotive exhaust, fuel cells, nano sensing and so on. For most catalytic applications, sintering of Pt NPs is undesired since the coalescence decreases the number of active sites of the catalyst. Herein we report the utilization of active oxide layers to encapsulate Pt NPs for CO oxidation. The active oxide coated catalysts have additional metal-oxide interfaces which may further improve the catalytic activity besides good sintering resistance. We use cobalt oxide, cerium oxide and nickel oxide as the active oxide encapsulations. Compared with aluminum oxide reference samples, these active oxides have been reported as much better materials with synergetic effect for Pt catalysts. The thickness of the metal oxide film is controlled by varying the number of ALD cycles. CO oxidation measurements were carried out in a micro flow reactor designed for planar model catalysts. Our results indicate that cobalt oxide coated Pt nanoparticles demonstrating the highest activity towards CO oxidation, and the optimal coating thickness is around 1nm. At the same time the coated catalysts have good thermal stability up to 750°C under atmospheric conditions. The enhancement of catalytic activity may originate from the active oxygen at the Pt/cobalt oxide interface, further Co (II) sites show better synergetic effect compared with Co (III) sites.

8:40am **TF+EN-WeM3 Passivation of Highly-doped c-Si Solar Cell Surfaces by Atomic Layer Deposition**

Bas van de Loo, Eindhoven University of Technology, Netherlands, *J. Melskens,* Eindhoven University of Technology, *G.J.M. Janssen,* ECN Solar Energy, *K.R.C. Mok, L.K. Nanver,* Delft University of Technology, *A.H.G. Vlooswijk,* Tempress Systems, *W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

Atomic layer deposition (ALD) of Al_2O_3 has been successfully implemented in silicon solar cell manufacturing, predominantly to passivate defects at the lowly-doped back surface of *p*-type solar cells. However, also for the passivation of highly-doped n^+ or p^+ type surfaces, present in e.g., high efficiency *n*-type solar cells, ALD films and stacks might become feasible. Yet, for such surfaces, the level of passivation strongly depends on the doping concentration and surface conditions. To allow for an even wider implementation of ALD-based passivation schemes in industrial solar cells, the work presented in this contribution aims to understand the passivation of highly-doped n^+ and p^+ type regions.

First of all, we observed that the passivation of boron-doped (p^+) Si surfaces highly depends on the doping process and the fixed charge density Q_f in the passivation layer. For instance, when a boron-rich layer (a B_xSi_y compound) was remained after the doping process, the surface passivation by ALD Al_2O_3 severely deteriorated. The formation of this undesirable layer could be avoided by using an oxidizing ambient during the drive-in of boron, although this results in a significant reduction in boron doping density at the surface. The latter impaired the level of passivation when Q_f was virtually zero, such as for ALD SiO_2/ Al_2O_3 stacks. Importantly, the level of surface passivation offered by ALD Al_2O_3 films remained high under these circumstances, due to the strong negative Q_f.

Next, for phosphorous doped (n^+) Si surfaces having surfaces densities of 10^{18}-10^{20} cm^{-3}, the passivation by dielectrics containing a negative Q_f such as ALD Al_2O_3, can be severely compromised, as the negative Q_f increases the minority carrier (i.e., hole-) concentration at and near the surface. Moreover, the negative Q_f can invert the n^+ Si surface, which triggers (undesirable) increased recombination at low injection levels and parasitic shunting. For those n^+ Si surfaces, it is demonstrated that ALD stacks such as SiO_2/ Al_2O_3 and HfO_2/ Al_2O_3 are promising alternatives to Al_2O_3 single layers, due to the absence of a negative Q_f. These stacks are particularly interesting from an industrial point of view, as they can make ALD viable for the passivation n^+ Si surfaces.

Lastly, ALD-based passivation schemes also have the potential to fully replace the heavily-doped n^+ and p^+ Si regions in solar cells. In this new field of 'passivating contacts', the significant recombination losses in the highly-doped regions can be avoided due to accurate band-alignment. Preliminary but promising results on novel electron-selective, passivating stacks of HfO_2 and TiO_2 by ALD will also be presented.

9:00am **TF+EN-WeM4 Low Temperature Plasma-Assisted Atomic Layer Deposition of TiO_2 Blocking Layers for Organo-Metal Halide Perovskite Solar Cells**

V. Zardetto, Eindhoven University of Technology, The Netherlands, *F. di Giacomo, G. Lucarelli, T.M. Brown, A. di Carlo, S. Licoccia, A. D'Epifanio,* University of Rome "Tor Vergata", Italy, *W.M.M. Kessels,* ***Mariadriana Creatore***, Eindhoven University of Technology, The Netherlands

Atomic layer deposition (ALD) offers accurate control in terms of film thickness, chemical and opto-electrical properties. This is extremely appealing for the novel class of mesoscopic solar cells (SCs), where the several interfaces between the absorber, charge transport layers and electrical contacts require the control of selected charge transfer and charge recombination processes.

Organo-metal halide perovskite SCs presently catalyze the interest in the PV community due to the remarkable increase in device performance in the last three years. Recently, thermal ALD processes have been applied for the deposition of TiO_2 blocking layers (BLs) in glass- based perovskite SCs[1]. Plasma-assisted ALD allows to extend the process window down to temperatures compatible with conductive plastic substrates. Therefore, in this work we investigate the role of plasma-assisted ALD TiO_2 BLs deposited on ITO/PET substrates for a $CH_3NH_3PbI_{3-x}Cl_x$ perovskite SC. The BLs are required to avoid the charge recombination process at the interface between the transparent conductive oxide layer and the perovskite and/or the hole transport layer. They have been prepared [2] in a remote plasma reactor (FlexAL^{TM}) at 150 °C using an heteroleptic alkylamido precursor $Ti(Cp^{Me})(NMe_2)_3$ exposure step alternated with an O_2 plasma exposure. Very low open circuit voltage (V_{OC} = 50mV) and efficiency (η = 0.01%) have been measured in the absence of the blocking layer. In this case, the analysis of dark current-voltage measurements revealed the lack of diode-like behavior and a significant exchange current (7 mA·cm^{-2}). The introduction of thin TiO_2 layers brought to an increment in all the photovoltaic parameters (J_{SC}, V_{OC} and FF), with a saturation in electrical efficiency for a TiO_2 thickness above 5.5 nm. The saturation in the anodic branch of the JV curve (V> 0) for ALD layers thicker than 5.5 nm points out that at this thickness the ALD layer is compact and therefore it suppresses the charge recombination processes. Dark current-voltage measurements have highlighted the decrease of exchange current and dark reverse current (V<0) up to three orders of magnitude with respect to the device without BL. The maximum performance of 9.2% on ITO-PET and 12.9% on ITO-Glass was achieved with 11 nm- thick TiO_2 BL, overcoming the efficiency achieved with conventional sol gel- deposited TiO_2 BLs (respectively, 4% and 8% on the two substrates).

[1] M. Grätzel, Nature Materials, 13, 838–842 (2014).

[2] F. Di Giacomo and V. Zardetto et al, Adv. Energy. Mater. 1401808 (2015)

9:20am **TF+EN-WeM5 Ultra-thin transition Metal Oxide-titania Alloy Coatings for Water Oxidation by Atomic Layer Deposition**

Olivia Hendricks, *C.E.D. Chidsey, P.C. McIntyre*, Stanford University

Synthesizing chemical fuels from solar energy requires a source of electrons. The most obvious choice for generating these electrons is the oxidation of water. The oxygen evolution reaction, however, is kinetically challenging, requiring significant overpotentials even with the best noble metal catalysts. At these positive potentials, preserving catalyst stability becomes a key concern. In industrial chlor-alkali electrolysis, which requires similarly positive potentials, the issue of catalyst durability was solved with the development of the dimensionally stable anode (DSA). Today's DSAs consist of a mixed TiO_2/RuO_2 coating prepared by thermal decomposition of appropriate precursors on a Ti substrate (Over, H. *Chem. Rev.*, 2012, 112, 3356). The TiO_2 imparts stability by preventing Ru dissolution, while the RuO_2 imparts sufficient activity and conductivity to the electrode. We report on the fabrication of an ultra-thin analogue to the DSA by atomic layer deposition (ALD) of ruthenium and TiO_2. We hypothesize that a conformal ALD coating of this type on nanostructured electrodes can optimize both the catalytic activity and durability for water oxidation while minimizing the use of transition metal components that have very limited Earth-abundance.

Both TiO_2 and Ru can be deposited simultaneously in our ALD reactor. Thus, by changing the relative number of ALD cycles for each precursor, we can achieve precise control of the catalyst content within the films. Preliminary results suggest that enhanced stability is achieved through the alloying process after annealing. The alloyed films also exhibit overpotentials that are competitive with pure ALD-Ru films deposited on a TiO_2 protective layer, even at relatively low Ru content. By decorating the TiO_2 surface with Ru ions at an optimal areal density, ALD alloying has the potential to achieve efficient catalysis of oxygen evolution from water while minimizing usage of the noble metal catalyst.

9:40am **TF+EN-WeM6 Atomic Layer Deposition of Nickel-Iron-Oxide Catalysts for Photoelectrochemical Splitting of Water**

Adrie Mackus, *K.L. Pickrahn, J.G. Baker, S.F. Bent*, Stanford University

The splitting of water to form hydrogen using sunlight as the source of energy has been actively researched in recent years to enable the production of green alternatives to fossil fuels. One of the main challenges in this technology is to develop a photoanode that (*i*) absorbs sunlight, (*ii*) has the ability to catalyze the oxygen evolution reaction (OER), (*iii*) is chemically stable in the aqueous electrolyte, and (*iv*) is made of earth-abundant materials. A strategy to synthesize an improved photoelectrochemical cell is to decouple these functions by conformally coating (e.g. by atomic layer deposition, ALD) a catalytic and protective layer on a nanostructured light-adsorbing material.[1]

In this work, we investigate ALD of NiO and $NiFe_xO_y$ films and their use as catalysts for the OER. The material $NiFe_xO_y$ was chosen because it is one of the most promising OER catalysts. The $NiFe_xO_y$ films were deposited using an ALD process that combines NiO ALD ($NiCp_2$, O_3) with Fe_2O_3 ALD ($FeCp_2$, O_3) in a supercycle. Alternatively, $NiFe_xO_y$ films were prepared by soaking ALD-grown NiO films in Fe-containing KOH electrolyte.[2] Using the latter approach, the best results were obtained when the electrode was preconditioned in Fe-poor KOH, causing the smooth and compact NiO film to partly exfoliate, which increases the number of electrochemically accessible Ni sites. Synchrotron-radiation X-ray diffraction was employed to investigate the phase of the material as a function of the deposition conditions. Moreover, the catalytic activity of the films for the OER was investigated by cyclic voltammetry (CV). It was found that incorporating Fe in the NiO films enhances the activity for OER significantly with a 10-fold increase of the turnover frequency.

1. T.M. Gür, S.F. Bent, and F.B. Prinz, *J. Phys. Chem. C*118, 21301 (2014)

2. Y.T. Chong, E.M.Y. Yau, K. Nielsch, and J. Bachmann, *Chem. Mater.***22**, 6506 (2010)

11:00am **TF+EN-WeM10 From Atom to Solid: The Structure of Amorphous ALD Thin Films and Nanolaminates**, ***Angel Yanguas-Gil***, Argonne National Laboratory **INVITED**

Atomic Layer Deposition is currently being used for a wide range of energy applications, such as photovoltaics, artificial photosynthesis, energy storage, and power semiconductor devices. In many cases the films are either very thin, well below 10 nm, or either doped or laminate materials, in which a second constituent is intercalated every few cycles.

Given the low deposition temperatures compared to other thin film processes, one of the key questions is how the microstructure of ALD materials differs from their bulk counterparts. This fundamental question of how atoms transition from isolated clusters or single monolayers to a local coordination environment characteristic of the bulk has important technological implications. Answering this question will allow us to better understand the performance of these materials as well as what makes ALD materials different, and in some cases better, to materials synthesized using other techniques.

In this talk I will discuss the impact that chemistry has on the properties and microstructure of very thin ALD films and nanolaminates of oxide dielectrics, semiconductors, and transparent conductors, comprising ZnO, HfO_2, and M:Al_2O_3 nanolaminates. By combining synchrotron X-ray characterization techniques such as X-ray Absorption Fine Structure (XAFS) and Pair Distribution Function (PDF) with in-situ techniques such as QCM and FTIR, my talk will focus on two particular problems: the evolution of coordination environment and the emergence of long-range order from the first monolayer and during the early stages of growth, and the impact that the interaction between dopant and host have in the microstructure of doped and laminate materials.

11:40am **TF+EN-WeM12 Inorganic Functionalization of Colloidal Quantum Dot Solar Cells through ALD Infilling**, ***Axel Palmstrom***, *P. Santra, S.F. Bent*, Stanford University

Colloidal quantum dot (CQD) solar cells are of great interest due to the tunable nature of the quantum dot light absorbers through size, composition and interface engineering, together with the potential for low-cost fabrication through solution processing techniques. Lead chalcogenide CQD devices have recently gained traction with rapidly improving efficiencies (>9%). Great strides have been made with organic ligand functionalization of the quantum dot surfaces to enhance CQD transport properties; however, these devices often suffer from poor long-term stability and are still limited by carrier lifetime and mobility. Atomic layer deposition (ALD), a technique that allows for conformal coating of nanostructured surfaces, has been used to improve stability and mobility of CQD solar cells by growing oxides within the quantum dot film. In this work, we explore the inorganic functionalization of CQD solar cells through combinations of ALD materials, including Al_2O_3, ZnO, NiO and other oxide materials, in thin (~30 nm) devices to ensure infilling throughout the entire device. With the proper choice of ALD oxide, short circuit current density and overall efficiency could be enhanced by 70% and 10% respectively relative to the non-infilled control CQD device. We will discuss the effects of ALD inorganic functionalization on surface passivation and carrier mobility as well as methods to implement ALD infilling on thicker devices in order to ultimately push the limits of CQD solar cell performance.

12:00pm **TF+EN-WeM13 Integrating Atomic Layer Deposited Lithium-Containing Thin Films for Lithium-ion Battery Applications**, *J. Cho*, ***Trevor Seegmiller***, *J. Lau, L. Smith, J. Hur, B. Dunn, J.P. Chang*, University of California at Los Angeles

Lithium-ion (Li-ion) batteries have demonstrated their performance in portable electronics for many years. Li-ion batteries also have the potential to be miniature power sources for microelectromechanical systems (MEMS) through 3-dimensional (3D) battery architectures. In order to fabricate a fully functional 3D Li-ion microbattery, an ultra-thin, highly conformal electrolyte layer is required to fully coat 3D electrodes. Lithium aluminosilicate ($Li_xAl_ySi_zO$, LASO), a solid oxide Li-ion conductor, synthesized by atomic layer deposition (ALD) is a promising electrolyte material for 3D battery applications due to its adequate ionic conductivity (1×10^{-7} S/cm) in thin film applications as well as improved electrode stability.

The self-limiting nature of ALD allows precise thickness and composition control when applied to complex metal oxides. This results in a highly conformal and pinhole-free coating on complex structures, including high aspect ratio 3D electrodes. Lithium tert-butoxide (LTB), trimethylaluminum (TMA), tris(tert-butoxy)silanol (TTBS), and tetraethylorthosilicate (TEOS) were precursors used to synthesize LASO by ALD. LASO films ranging in thickness from 6 to 12 nm exhibited Li-ion conductivity from 8.2×10^{-8} to 1.4×10^{-9} S/cm. The LASO films were also deposited on anode and cathode materials for evaluating their integration into solid state Li-ion batteries. A Li-ion half-cell consisting of LASO-coated 2D carbon anode showed reversible electrochemical behavior with coulombic efficiency reaching 98%.

Current research on Li-ion batteries is directed at creating next generation anode materials. Both silicon and germanium have received considerable study due to their high theoretical volumetric capacity (8444 A h L^{-1} for $Li_{15}Si_4$ and 7366 A h L^{-1} for $Li_{15}Ge_4$ respectively). Upon lithium intercalation, however, these anode materials undergo large volumetric expansion (~300% for Si) which compromises their mechanical integrity. We have started to carry out *in situ* transmission electron microscopy (TEM) studies in which the structural effects of lithium intercalation and deintercalation on silicon/germanium (Si/Ge) alloy nanowires conformally coated with LASO electrolyte are characterized . These *in* situ TEM studies show 40% radial expansion of the $Si_{0.4}Ge_{0.6}$ alloy upon lithium intercalation, and morphological changes upon deintercalation, with the LASO film preserved on the nanowire.

Thin Film
Room: 114 - Session TF+SS-WeM

ALD Surface Reactions and Precursors
Moderator: Sean Jones, National Science Foundation (NSF), Paul Poodt, Solliance/TNO

8:00am **TF+SS-WeM1 High Performance Precursors for Atomic Layer Deposition of Silicon Containing Films**, ***Anu Mallikarjunan***, Air Products and Chemicals, Inc. **INVITED**

Conformal and continuous silicon containing films produced by Atomic Layer Deposition (ALD) are enabling novel processing schemes and integrated device structures. The increasing drive towards lower temperature processing requires new precursors with even higher reactivity. A systematic method for identification of high performance precursors is thus very desirable, and needs to incorporate fundamental understanding of precursor chemistry, surface reactions; and relationships between precursor structure and deposited films. The overall approach accordingly relies on integrating molecular and surface reaction modeling, the ability to synthesize stable precursors with reactive groups, in-situ surface studies, and thin film deposition testing. To illustrate this approach, two case-studies will be discussed in this presentation: silicon oxide and silicon nitride ALD. In both cases, a representative monoaminosilane $(R^1R^2N)SiH_3$ called di - sec- butylaminosilane (DSBAS) will be studied. The impact of changing the precursor structure will also be discussed.

8:40am **TF+SS-WeM3 Amorphous In_2O_3 and Sn-doped In_2O_3 Layers by ALD Prepared using Trimethyl Indium and Ozone**, ***Anil Mane***, *A. Allen*, Argonne National Laboratory, *R. Kanjolia*, SAFC Hitech, *J. Elam*, Argonne National Laboratory

Abstract:

Among the transparent conducting oxides (TCOs), Indium oxide (In_2O_3) possesses a wide band gap of 2.9 Ev at room temperature yielding high optical transparency and also exhibits good chemical stability. When doped with tin to form Indium tin oxide (ITO), the electrical conductivity increases greatly allowing this material to be used in a wide range of applications including touch screens displays, light-emitting diodes, liquid crystal displays, and sensors. Further amorphous TCOs have several advantages over their crystalline microstructures e.g. lower temperatures deposition which tend to simplify the deposition methods for mainly for plastics for flexible electronics. The lack of grain boundaries in amorphous materials, isotropic nature allows a simpler scheme for uniform etching with lower surface roughness. Unlike crystalline TCOs, the amorphous TCOs electrical and optical are also strongly influenced by the oxygen content of the films. As ALD offers the potential to deposit ITO over large areas at low temperature with high uniformity to address some of these applications, but the viability of this method hinges on developing a robust In_2O_3 ALD process. Trimethyl indium (TMIn) is an attractive economical precursor for In_2O_3 ALD because it offers the advantages of a high vapor pressure and availability in high volume.

In this study we examined the ALD of In_2O_3 using alternating exposures to TMIn and different oxygen sources: O_3 (ozone), O_2, H_2O, and H_2O_2. We first used in situ quartz crystal microbalance (QCM) and mass spectrometry measurements to evaluate the effectiveness of the different oxygen sources and found that only ozone yielded sustained growth. These measurements also provided details about the In_2O_3 growth mechanism and enabled us to verify that both the TMIn and the O_3 surface reactions were self-limiting. Next, we prepared ALD In_2O_3 films on a variety of substrates and characterized them using X-ray diffraction, UV-vis. Spectrometry, spectroscopic ellipsometry, X-ray photoelectron spectroscopy, Hall probe measurements, scanning electron microscopy, and atomic force microscopy. We found that at deposition temperatures of 100-200^{o}C the amorphous growth per cycle was nearly constant at ~0.4 Å/cycle and the films were dense and pure. At higher growth temperatures the In_2O_3 growth rate increased due to thermal decomposition of the TMIn. We succeeded in doping the amorphous In_2O_3 films with tin by substituting tetrakis-(dimethylamino) tin for the TMIn in a fraction of the growth cycles and observed that the electrical conductivity improved substantially in these films.

9:00am **TF+SS-WeM4 Towards Organic Electronics: Atomic Layer Like Deposition of ZnS and ZnO on Organic Thin Films**, *Z. Shi, **Amy Walker***, University of Texas at Dallas

We discuss our recent studies of atomic layer like deposition (ALLD) of ZnS and ZnO on organic thin films using diethyl zinc (DEZ) as the zinc source. This work has important applications in photovoltaics, molecular and organic electronics, sensing, photonics and other technologies. We show that a detailed understanding of the reaction pathways is critical for controlling the properties of ZnO and ZnS films grown by ALD. For both ZnO and ZnS ALLD, the growth rates on –COOH terminated SAMs are approximately 10 % lower than on –OH terminated SAMs. As expected on −OH terminated SAMs, the DEZ reacts with the hydroxyl group. However, on –COOH terminated SAMs DEZ reacts with both the carbonyl and hydroxyl bonds present leading to the formation of a ketone rather than deposition. Further, the composition of the deposited layer and its growth can be affected by the functionality of the surface. For ZnO ALLD, on-COOH terminated SAMs XPS indicates that the initial composition of the layer is similar to $Zn(OH)_2$. In contrast on –OH terminated SAMs the deposited layer is always composed on ZnO. The growth of the layer also appears to be different. On –COOH terminated SAMs, the layer growth is more two dimensional (layer-by-layer) while on –OH terminated SAMs, the growth appears to proceed via the formation of islands.

9:20am **TF+SS-WeM5 AlF_3 Atomic Layer Deposition or Al_2O_3 Atomic Layer Etching from Sequential Exposures of Trimethylaluminum and HF**, ***Jaime DuMont**, Y. Lee, S.M. George*, University of Colorado at Boulder

Sequential exposures of $Al(CH_3)_3$ [trimethylaluminum (TMA)] and HF can lead to either AlF_3 atomic layer deposition (ALD) or Al_2O_3 atomic layer etching (ALE). The observation of AlF_3 ALD or Al_2O_3 ALE depends on temperature and pressure. AlF_3 ALD occurs at lower temperatures and higher pressures. Al_2O_3 ALE of an initial Al_2O_3 film occurs at higher temperatures and lower pressures. The AlF_3 ALD or Al_2O_3 ALE were investigated using *in situ* Fourier transform infrared (FTIR) spectroscopy and quartz crystal microbalance (QCM) measurements.

The FTIR analysis observed AlF_3 ALD or Al_2O_3 ALE by measuring the absorbance gain of Al-F stretching vibrations in AlF_3 or the absorbance loss of Al-O stretching vibrations in Al_2O_3. At lower temperatures, the HF exposures react with the underlying Al_2O_3 surface to form AlF_3 and HF molecules on the surface. TMA molecules subsequently react with HF on the surface to yield $AlF(CH_3)_2$ surface species. $AlF(CH_3)_2$ is then converted to AlF_3 with the next HF exposure producing AlF_3 ALD. At higher temperatures, the HF exposures react with the underlying Al_2O_3 surface to form AlF_3 and fewer HF molecules absorb on the surface. TMA then accepts fluorine from AlF_3 to form $AlF(CH_3)_2$ which desorbs from the surface and leads to etching of the initial Al_2O_3 film.

The effect of pressure was also explored by adjusting the N_2 carrier gas flow from 0-150 sccm to vary the background pressure from 30 mTorr to 1.6 Torr. These FTIR experiments revealed that the transition from AlF_3 ALD to Al_2O_3 ALE occurred at higher temperatures for higher background pressures. The higher pressures apparently produce a “cage effect” and increase the lifetime of the $AlF(CH_3)_2$ surface species that leads to AlF_3 ALD. The QCM experiments measured an AlF_3 ALD growth rate that progressively decreased at higher temperatures and went negative at >250°C when TMA and HF etched the AlF_3 or Al_2O_3 films.

9:40am **TF+SS-WeM6 A Comparison of Water Delivery Methods for Atomic Layer Deposition**, ***Tariq Ahmido**, W.A. Kimes, B.A. Sperling, J.E. Maslar*, NIST

Water is frequently used as an oxygen source for atomic layer deposition (ALD) of metal oxides. However, water exhibits a relatively high vapor pressure at room temperature and readily adsorbs on reactor surfaces. These characteristics can make it difficult to reproducibly control water delivery during ALD, particularly when small quantities are desired. The focus of this work is characterizing and comparing three different methods of water vapor delivery in an effort to identify techniques for ensuring reproducible delivery of water vapor quantities. For this investigation, three methods of water injection were compared. The first method utilizes a needle valve between the water reservoir and the water injection valve (the valve that controls the water allowed into the delivery line to the reactor). This method is commonly employed for research grade reactors as the use of an adjustable orifice permits the water flow rate to be varied. However, control of small water quantities can be difficult due to the buildup of water vapor between the needle valve and the water injection valve. The second method overcomes this control limitation by utilizing a pump to vent water vapor from the volume between the needle valve and injection valve prior to injection into the delivery line. This method provides a high degree of control at the cost of added complexity and expense. The third method utilizes a laser-drilled orifice in a VCR gasket as the flow-controlling orifice. This method is simple and inexpensive, however, water flow rates cannot be adjusted without changing the orifice. The performance of these three water injection methods was characterized using an optical water mass flow meter (MFM) that has been developed to rapidly quantify water vapor. This MFM was based upon a wavelength modulation spectroscopic technique utilizing a near-infrared diode laser. This MFM permits quantitative comparison of the performance of these three water injection methods, allowing a potential user to identify method suited to a particular application.

11:00am **TF+SS-WeM10 Stoichiometric Dependence of the Interface of HfO_2 ZrO_2, TiO_2, Ta_2O_5 and La_2O_3 on Si (100) by ALD**, ***Pierre Mani***, Universidad Autónoma de Ciudad Juárez-IIT, Mexico, *E. Lopez*, Universidad Autónoma de San Luis Potosí, Mexico, *H. Leos*, Universidad Autónoma de Ciudad Juárez-IIT, Mexico, *H. Hernandez*, Universidad Autónoma de San Luis Potosí, Mexico, *J.A. Hernandez, J.R. Farias, J.T. Elizalde*, Universidad Autónoma de Ciudad Juárez-IIT, Mexico, *M.A. Melendez*, CINVESTAV, Mexico, *M.A. Vidal*, Universidad Autónoma de San Luis Potosí, Mexico

A systematic analysis was performed to determine the characteristic times of surface coverage of oxidant-agent on silicon substrates (100) by the atomic layer deposition (ALD) method in order to ensure the saturation of the surface substrate for growth. The aperture-times of the precursors have been studied due to stoichiometric impact of the layers and also at the interface. The numbers of cycles were critical for the interface formation at the early stage growth. This work emphasizes in the study and analysis between interface of high k dielectric layer and amount of cycles as function of layers and stoichiometric interface. Previous works complement with results obtained in study the growth of hafnium oxide and titanium oxide by atomic layer deposition (ALD) demonstrating the close relationship between the thickness and composition of the interface layer with the number of cycles performed by the ALD and with the aperture-time of the precursors. This analysis shows a base that will allow create HfO2 ZrO2, TiO2, Ta2O5, La2O3 nanofilms with optimal characteristics.

11:20am **TF+SS-WeM11 In-situ Infrared Study of Atomic Layer Deposition of Molybdenum Nitride using Bis(tert-Butylimido)-Bis(dimethylamido) Molybdenum and Hydrazine**, ***Abraham Vega**, C.E. Nanayakkara*, The University of Texas at Dallas, *G. Liu, R. Kanjolia*, SAFC Hitech, *Y.J. Chabal*, The University of Texas at Dallas

Molybdenum nitride films have properties such as high hardness, high melting point, good chemical stability and high conductivity, which makes them suitable for a wide range of technological areas, as diffusion barriers or interconnections in microelectronics and even as catalysts in fuel cells. Molybdenum nitride films have been deposited by variety of techniques, such as chemical vapor deposition, magnetron sputtering, and atomic layer deposition among others.

For atomic layer deposition of molybdenum nitride, molybdenum complexes containing alkylamido and alkylimido ligands are being considered as potential molybdenum precursors. A notable advantage is that they do not produce corrosive byproducts compared to halide based transition metal precursors.[1] A uniform growth has been achieved in the range 260 – 300 ^{0}C with bis(tert-butylimido)-bis(dimethylamido)molybdenum when used with NH_3 as a co-reactant.[1]

In this study, *in-situ* IR and X-ray photoelectron spectroscopies are used to investigate ALD of bis(tert-butylimido)-bis(dimethylamido)molybdenum and hydrazine an alternative for NH_3 as co-reactant for molybdenum nitride deposition on pre-annealed, oxidized and OH-terminated Si(100) surfaces. While bis(tert-butylimido)-bis(dimethylamido) molybdenum is expected to react with two surface OH groups leaving one amino groups with further reaction with hydrazine leading to a NH_x-terminated surface, the details of the reactions have not been explored, hence the importance of *in-situ* IR spectroscopy.

Bis(tert-butylimido)-bis(dimethylamido) molybdenum reacts with surface Si-OH groups (loss at 3740 cm^{-1}) to form the expected $(O)_2$-Mo=(N-tBu)$_2$structure, as evidenced by broad band from various CH_x stretch bands in the 2900 cm^{-1} region and stretching of CN bonds at 1240 cm^{-1}, respectively. The first hydrazine pulse leads to a loss of tBu vibrational bands [at 2900 and 1240 cm^{-1}]. The steady state ALD process is characterized by tBu removal by hydrazine and formation of NH_x groups driving the ALD process. A clear ligand exchange is observed at deposition temperatures of 225, 250 and 275 °C for 30 cycles. The ALD window for this process was found to be between 225 and 275 °C, with low carbon content determined by XPS, which is lower than the window when using NH_3 (260-300 °C) instead of hydrazine. No growth is observed above 300 °C, and very poor quality films are obtained at 200°C.

This work confirms the reactivity of bis(tert-butylimido)-bis(dimethylamido) molybdenum with OH-terminated surfaces at low temperatures and illustrates the role of the co-reactant on the thermal window and the quality of the resulting molybdenum nitride films.

1. Chem. Mater., Vol. 19, No. 2, 2007

11:40am **TF+SS-WeM12 Atomic-Layer-Deposited In_2O_3:H Transparent Conductive Oxides: How to Achieve the Best Possible Carrier Mobility**, ***Bart Macco****, Eindhoven University of Technology, Netherlands, *H.C.M. Knoops,* Oxford Instruments Plasma Technology, UK, *M.A. Verheijen, W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

Recently, we have reported on an atomic layer deposition (ALD) process to prepare H-doped indium oxide (In_2O_3:H) transparent conductive oxides (TCOs) with an extremely high carrier mobility (138 cm^2/Vs) and low resistivity (0.27 mΩcm) at low processing temperatures (<200 ºC) [1]. This high carrier mobility is especially promising for silicon heterojunction solar cell applications, as it allows for a low resistivity at low carrier density, thereby nullifying parasitic free carrier absorption in the infrared. Here we focus on new insights into the physical mechanisms during the preparation process and explain how such high mobility can be obtained through analysis of the electron scattering and doping mechanisms.

The preparation starts with ALD of In_2O_3:H at 100 ºC using InCp, H_2O and O_2 as growth precursors. The films are amorphous, although a low density of very small crystallites is present. Subsequently the films are crystallized by annealing at 150-200 ºC. Electron microscopy reveals that crystallization proceeds from grain growth from the pre-existing crystallites without additional nucleation, which makes the final grain size and optoelectronic properties independent of annealing temperature. The resulting crystals extend over the film thickness of 75 nm and have a typical lateral size of a few hundred nm. Analysis of the grain growth by electron microscopy shows a thermally activated behavior, with an activation energy of 1.4 eV.

A combination of temperature-dependent Hall measurements and spectroscopic ellipsometry has been employed to distinguish between the various scattering mechanisms and dopants in crystallized In_2O_3:H films. Key results include the fact that carrier mobility is only limited by ionized impurity and phonon scattering processes and that other extrinsic defect scattering such as neutral impurity and grain boundary scattering can be neglected. Since only unavoidable scattering processes play a role, this means that this TCO has the highest possible mobility at this carrier density. The analysis also excludes a significant contribution from doubly charged donors (i.e. oxygen vacancies), and the source of doping is confirmed to be singly charged H. Furthermore, by comparison of the absolute H-concentration and the carrier density in crystallized films, it is deduced that <4 % of the incorporated H is an active dopant in crystallized films. Therefore, it can be concluded that inactive H atoms do not contribute to defect scattering, which explains why In_2O_3:H films are capable of achieving a much higher carrier mobility than conventional In_2O_3:Sn films.

[1] Macco et al., *P.S.S. - Rapid Res. Lett.*, DOI: 10.1002/pssr.201409426

12:00pm **TF+SS-WeM13 Mechanical Property and Corrosion Resistance Evaluation of CrVN and CrSiN Thin Films Grown by a Hybrid High Power Impulse Magnetron Sputtering and Radio Frequency Sputtering Technique**, ***Jyh-Wei Lee***, *C.Y. Cheng, P.W. Chang,* Ming Chi University of Technology, Taiwan, Taiwan, Republic of China, *B.S. Lou*, Chang Gung University, Taiwan, Taiwan, Republic of China

High power impulse magnetron sputtering (HIPIMS) is a novel coating technology, which is characterized for its high peak power density to achieve unique thin film properties, such as high hardness, good adhesion and tribological performance. The aim of this work was to systematically study the microstructure, mechanical properties and corrosion resistance of CrVN and CrSiN coatings fabricated by a hybrid high power impulse magnetron sputtering and radio frequency sputtering technique. The experimental results showed that the peak power density increased linearly as the duty cycle decreasing from 5% to 2.5%. As compared with the CrVN coating, the higher hardness and better corrosion resistance were obtained for the CrSiN coatings, which can be attributed to their denser microstructures fabricated using the HIPIMS technology under optimal duty cycle and pulse frequency in this work. Effects of Vanadium and Silicon elements on the microstructure, mechanical and electrochemical properties of CrVN and CrSiN coatings were also discussed.

Vacuum Technology
Room: 230B - Session VT-WeM

Accelerator and Large Vacuum Systems
Moderator: Yulin Li, Cornell University, Lily Wang, Los Alamos National Laboratory

8:00am **VT-WeM1 MAXIV Vacuum System: From Design to Operation**, ***Eshraq Al-Dmour***, *M. Grabski, J. Ahlbäck, P. Fernandes Tavares, C. Pasquino*, Max IV Laboratory **INVITED**

MAXIV facility is under commissioning in Lund-Sweden. The facility consists of full energy Linac, two electron storage rings operating at 1.5 GeV and 3 GeV and a short pulse facility. The 3 GeV storage ring is 528 m in circumference, and has compact magnets design with small magnet apertures, as a result, the chambers inside diameter is also small (22 mm), so the conductance of the vacuum chambers is low and lumped pumps are ineffective. In order to provide the desired vacuum level (less than 1e-9 mbar) distributed pumping which has been realized by the use of non-evaporable getter (NEG) coating of the chamber walls was implemented. In addition, the vacuum chambers should absorb the heat from synchrotron radiation (SR) as an antechamber is difficult to realize, to solve this, the chambers are made from Silver bearing oxygen free (OFS) copper and the walls work as distributed absorbers where distributed cooling is used at the location where the SR hits the wall. The design, production, installation and conditioning of the vacuum system were a challenge, and therefore they are presented here.

8:40am **VT-WeM3 Construction Status of the SuperKEKB Vacuum System**, ***Yusuke Suetsugu***, *K. Kanazawa, K. Shibata, T. Ishibashi, H. Hisamatsu, M. Shirai, S. Terui*, KEK-High Energy Accelerator Research Organization

The SuperKEKB, the upgrade project of KEKB, is an electron-positron collider with asymmetric energies, that is, 7 GeV electrons and 4 GeV positrons. The goal luminosity is $8x10^{35}$ $cm^{-2}s^{-1}$, approximately 40 times higher than that achieved in the KEKB. The construction of the new vacuum system for the SuperKEKB has been in progress since 2010, as a key item of the upgrade. Most of the vacuum components, especially in the positron ring, are newly fabricated to manage the electron cloud effect (ECE), and to reduce beam impedance, which are essential to keep the low-emittance beams stable even for high beam currents. The design and the manufacturing of the major vacuum components, including beam pipes, bellows chambers, gate valves, vacuum pumps and so on, have been completed. Approximately 1240 new beam pipes were made of aluminum-alloy or pure copper depending on the intensity of the irradiated synchrotron radiation. They basically have two antechambers at both sides of a central beam channel. The main pump at arc sections of the ring is a strip-type NEG installed in one of the antechambers. Approximately 1130 NEG modules were prepared with various lengths of from 0.7 to 3 m consisting of three NEG strips. New bellows chambers and gate valves have basically a comb-type RF-shield and have the same cross sections to the connecting beam pipes. Countermeasures against the ECE, such as the coating of TiN film, the grooved surface, the clearing electrode and so on, were prepared for the beam pipes of the positron ring. All of aluminum-alloy beam pipe have TiN coating inside to reduce the secondary electron yield. Approximately 150 beam pipes for dipole-type magnets have grooved structure at top and bottom of the inner surface. Beam pipes for wiggler magnets have 116 clearing electrodes inside in total. The installation of these components into the KEKB tunnel has almost finished. The MO-type flanges, which have structurally little step inside, were adopted to the connection flanges between the beam pipes and the bellows chambers. The air-leak rate at the first fastening was less than 5 % out of more than 5000 times fastening in total during the pre-baking, the TiN coating and the connection in the tunnel. The final activation of NEG pumps in the tunnel has finished approximately 70 % of the ring until October. After the NEG activation, the average pressures decreased to on the order of 10^{-8} Pa, where the beam pipes were not baked in situ. The vacuum system will be ready in next January, 2016. The construction status SuperKEKB vacuum system, including various experiences during the construction stage, will be reported.

*** TFD James Harper Award Finalist**

9:00am **VT-WeM4 Commissioning of the 3 GeV TPS Accelerator Vacuum System**, ***Gao-Yu Hsiung****, Y.C. Yang, H.P. Hsueh, L.H. Wu, C.M. Cheng, C.K. Chan, J.R. Chen*, National Synchrotron Radiation Research Center, Taiwan, Republic of China

The Taiwan Photon Source (TPS), a 3 GeV synchrotron light source composed of a booster synchrotron and the electron storage ring concentrically installed in the same tunnel, has been completed the construction and the installation in July 2014. Then the commissioning of the booster has been started and reached to the goal of 3 GeV full-energy-injections on Dec.17. After tuning the beam parameters, the electron beam was stored at 1 mA beam current, extracting the first synchrotron light, and raised to 4.5 mA stored with few minutes beam life time on Dec. 31 2014. The beam-cleaning process for mitigating the significant photon-stimulated-desorption (PSD) outgas inside the storage ring is one of the major purposes of the commissioning. The pressure in the beam duct was kept under 1E-6 Pa that limited the increase of beam current and the consequent upper bound of the Bremsstrahlung radiation level through the beam-cleaning. After three-months commissioning that has achieved the accumulated beam dose of 30 Ampere-hours, the average pressure was reduced to ~ 1.2E-7 Pa at 100 mA of stored beam current with life time of ~ 6 hour. Besides the vacuum conditioning, the beam emittance of 1.6 nm-rad approached to the goal has been demonstrated. In this paper, the concept about the high efficient beam-cleaning process and the progress of the commissioning for the TPS will be described.

9:20am **VT-WeM5 Construction, Installation, and Commissioning of TPS Booster Vacuum System**, ***Hsin-Pai Hsueh****, C.M. Cheng, S.N. Hsu, G.Y. Hsiung, J.R. Chen*, National Synchrotron Radiation Research Center, Taiwan, Republic of China

For better performance and more efficient operation of today's storage ring of electron synchrotron radiation facilities, it is essential to have a good booster vacuum system to start with. The ultrahigh vacuum system for the electron booster ring of the 3GeV Taiwan Photon Source accelerator has been constructed since 2010, and then installed and commissioned since 2014. TPS booster is a 496.8m long stainless steel vacuum system and currently the largest of its kind in the world. Although low impedance consideration is not critical in a booster vacuum system, the tight dimension and other demanding engineering tolerances do show their criticalness in the construction, installation, and commissioning phases. During construction, some of the original ideas have been modified due to these given tight tolerances. It is even more demanding as we found in the commissioning phase and a lot of actions have been taken to make commissioning process possible. The original design, the modifications in both the construction and commissioning phases will be described in this paper.

9:40am **VT-WeM6 Design of a 250 KV DC Electron Gun Operating at Cryogenic Temperature**, ***Xianghong Liu****, I. Bazarov, B.M. Dunham, V.O. Kostroun, H. Lee*, Cornell University

A photocathode DC electron gun is being built in our laboratory for ultrafast electron diffraction experiments. It is designed to operate at voltages up to 250 KV, with a maximum electric field of 12 MV/m in the cathode – anode gap. An inverted ceramic insulator is used for the high voltage insulation, making the gun relatively compact. In order to reduce the mean transverse energy of the electrons emitted from the photocathode, and hence increase the coherent length of the electron beam at diffraction, the photocathode is operated at 20 K instead of room temperature. A stainless steel thin wall tube connects the cathode holder to the insulator; it minimizes the heat load through conduction while providing a rigid support for the cathode holder. The cathode holder is cooled by a cold head through a sapphire rod of 225 mm length. The sapphire rod provides both sufficient electrical insulation and excellent thermal conduction at the temperature of interest. A load-lock system is attached to the back of the gun chamber for loading the photocathode to the gun. Photocathodes are transported into and out of the system through a vacuum suitcase. The load-lock system also provides storage for multiple photocathodes. The decay of the quantum efficiency of the photocathode is dominated by the existence of residual gases in the gun chamber, and thus vacuum level of 1x10-11 Torr or better is required to prolong the lifetime of the photocathode. The chamber is pumped by NEG pumps and ion pumps. We'll describe details of the design and report initial test results.

11:00am **VT-WeM10 Introduction to Tri Alpha Energy's Fusion Concept, Vacuum Requirements and Performance of Our Current C2U Machine**, ***Alan Van Drie***, Tri Alpha Energy

Tri Alpha Energy (TAE) is researching a novel fusion concept of energetic ions magnetically trapped as large orbits in a Field Reverse Configuration plasma (FRC). C2 and C2U are the previous and current generation machines that have pushed and continue to push our understanding of FRC plasmas, energy levels, durations, control, and engineering required toward an energy generating machine. C2 was operated between 2008 and 2014, followed by its completed upgrade to C2U in early 2015. C2 and C2U are both linear vessels (~20m long, ~17m^3 volume, low 10^{-9} Torr pressures) with many attached sub systems such as 1.8 MW neutral beam sources (10 MW total injected power into the plasma) and a plethora of diagnostics. The talk will first give an overview to TAE's concepts and C2U, followed by a discussion of the physics that drive the vacuum requirements, such as wall recycling, ion-neutral losses, divertor gas loads and how we solved many of the technical vacuum challenges in order to meet our performance goals.

11:20am **VT-WeM11 Vacuum Architecture of an Extreme Ultra-Violet Exposure System**, ***Freek Molkenboer****, N.B. Koster, A.F. Deutz, D.J. Naron*, TNO Technical Sciences, Netherlands

TNO is designing and building an Extreme Ultra-Violet (EUV) exposure system capable of exposing samples and 6" EUV masks with high EUV power and intensity. This system will be named EBL2.

EBL2 will be suited for characterizing and analysing phenomena such as carbon growth on EUV masks, oxidation of multilayer optics, as well as investigating the physics and effects of EUV-induced plasmas.

EBL2 contains an EUV Beam Line, in which samples/EUV masks can be exposed to EUV radiation in a flexible gas environment, with UHV background vacuum quality. Gases such as H_2, XCDA and H_2O can be added in a controlled fashion to create a customized environment for the exposure at hand.

Attached to this Beam Line is an XPS system, which can be reached from the Beam Line via an in-vacuum transfer system. This enables surface analysis of exposed samples/masks without breaking vacuum. Automatic mask handling with dual pods is foreseen so that exposed EUV mask will still be usable in EUV lithography tools to assess the imaging impact of the exposure.

Qualification of the setup is expected to start Q1 2016. After completion, this unique facility will be open for external customers and other research groups.

This presentation will focus on the vacuum architecture and design implementations of the EBL2 system to meet all the stringent vacuum requirements.

Wednesday Lunch, October 21, 2015

Exhibitor Technology Spotlight
Room: Hall 1 - Session EW-WeL

Exhibitor Technology Spotlight Session
Moderator: Dennis Sollon, Kurt J. Lesker

12:40pm **EW-WeL2 Wet Cell II for Analysis at the Liquid Vacuum Interface***, **Junhang Luo***, SPI Supplies

The liquid interfaces are very active and important for environmental, biological, and industrial processes. However, most surface analysis instrument are vacuum based and the rapid liquid evaporation makes in-situ analyzing liquid surface extreme challenge. Wet Cell II offers a simple solution for scientists and researchers to directly analysis of liquids at the molecular level in a vacuum environment with minor cost. As a lab-on-a-chip device, Wet Cell II can be straightforwardly adaptable to many different analytical platforms, including scanning electron microscopy (SEM) and time-of-flight secondary ion mass spectrometry (TOF-SIMS). Wet Cell II requires little or no sample preparation and only consumes a few drops of liquid. Typical applications include microbiology, liquid surface chemistry, drug delivery & reaction, and energy storage, etc.

1:00pm **EW-WeL3 Relative Permeation Performance of O-ring Seals Using DuPont Test Methodology***, **Mark Heller***, DuPont™ Kalrez®

As Large Scale Integration (LSI) Devices become more advanced, feature sizes are continuing to get smaller and the associated film thicknesses deposited are reaching atomic levels. As a result, the outgassing and permeation characteristics of elastomeric seal materials used in high temperature and high vacuum processes are important factors that can influence film uniformity, quality and consistency. DuPont Performance Polymers (DPP) has developed a practical test methodology for comparing relative permeability characteristics of O-ring seals under high vacuum conditions using a Quadrupole Mass Analyzer (QMA) and Ionization Vacuum Gauges. The method will be discussed and a sampling of data generated for various O-ring materials / compositions will be reviewed.

1:20pm **EW-WeL4 Advances in Bellows Electroforming***, **Berl Stein***, NiCoForm

Improved mechanical properties of NiCoForm's nickel-based alloy, NiColoy®, broaden the appeal of electroformed bellows. Newer manufacturing techniques shorten lead times and reduce cost of custom, as well as standard bellows. Proprietary electrojoining, corrosion protection and multi-ply technologies deliver industry-leading performance in net-shape electroformed, ready-to-use components.

1:40pm **EW-WeL5 PREVAC's Solutions for Helium Temperature Sample Manipulation and Related Sample Transferring Systems***, **Adam Dziwoki***, PREVAC sp. z o.o., Poland

The wide range of temperatures is the key point for number of analytical techniques. We are able to cool down and stabilise the temperature of the sample in 5-6 axes manipulators below 10K. Our latest upgrade in helium manipulator is the possibility of the sample heating and extension of the tilt range implemented without any impact on continuous rotation. If you need a solution for fast and reliable transfer between several chambers in UHV conditions we invite you to check in person a manual or motorised solutions for Radial Distribution Chamber. Thanks to it the spectroscopy, deposition and microscopy chambers with all auxiliary chambers can be connected together.

2:00pm **EW-WeL6 Variations on Vacuum Baking for MEMS Processing**, ***William Moffatt***, *K. Sautter*, Yield Engineering Systems, Inc.

Yeld Engineering Systems' latest series of ovens are essential tools for Semiconductor, MEMS and Wafer-level packaging (WLP) processes. The full presentation will explain the technical process involved for each tool in the YES-VertaSeries: The YES-VertaCure automated, high temperature cure series of ovens helps achieve total environmental control to increase yields and extend device performance.

Applications

- Polyimide cure
- BCB cure
- Low temp polymers cure
- Copper anneal

The YES-VertaCoat automated, silane vapor deposition system is designed for today's most advanced MEMS and semiconductor process applications. Whether it's precise surface modification to reduce stiction for MEMS devices or a thin copper diffusion barrier layer in an advanced semiconductor device, the capability to use a large number of different organosilanes provides the ability for precise surface modification.

Applications

- Wafer dehydration
- Surface tension modification
- Copper diffusion barrier

The YES-VertaVac series of automated high vacuum ovens ensures moisture and hydrogen removal using high vacuum (10-5) and high temperature (up to 450°C). Our patented nitrogen purge precedes process ramp and creates a successful procedure for improved MEMS lifetime and performance.

Applications:

- Wafer dehydration
- Getter activation
- Metal annealing

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 MoS_2**, ***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.

[1] O. V. Yazyev and Y. P. Chen, Nature Nanotechnology **9**, 755 (2014).

[2] O. V. Yazyev and S. G. Louie, Phys. Rev. B **81**, 195420 (2010).

[3] Y. Tison *et al.,* Nano Lett. **14**, 6382 (2014).

[4] O. V. Yazyev and S. G. Louie, Nature Materials **9**, 806 (2010).

[5] J. H. Chen *et al.,* Phys. Rev. B **89**, 121407(R) (2014).

[6] F. Gargiulo and O. V. Yazyev, Nano Lett. **14**, 250 (2014).

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[8] O. Lehtinen *et al.,* ACS Nano **9**, 3274 (2015).

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 3*d* 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.

This work was supported in part by NSF Award No. 1407765, the Center for Low Energy Systems Technology (LEAST), one of six centers supported by the STARnet phase of the Focus Center Research Program (FCRP), a Semiconductor Research Corporation program sponsored by MARCO and DARPA, and by the Southwest Academy on Nanoelectronics (SWAN) sponsored by the Nanoelectronic Research Initiative and NIST.

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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.

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

1 K. W. Clark, et al., *ACS Nano***7**, 7956 (2013).

2 K. W. Clark, et al., *Phys. Rev. X***4**, 011021 (2014).

3 L. Liu, et al., *Science***343**, 163 (2014).

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)

2. Jiayu Wan, Feng Gu, Wenzhong Bao, et al. Nano Letters, 2015, DOI: 10.1021/acs.nanolett.5b00300.

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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*** NSTD Student Award Finalist**

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Actinides and Rare Earths Focus Topic
Room: 230A - Session AC+AS+MI-WeA

Chemistry and Physics of the Actinides and Rare Earths
Moderator: Ladislav Havela, Charles University, Prague, Czech Republic

2:20pm **AC+AS+MI-WeA1 High Resolution X-ray Absorption Spectroscopy as an Advanced Tool for Structural Investigations of Actinides**, ***Tonya Vitova***, Karlsruhe Institute of Technology, Germany **INVITED**

Advanced spectroscopy methods, which provide precise speciation, redox state, and electronic structure information, are needed to benchmark and drive improvement of geochemical/thermodynamic modeling and quantum chemical computational methods. The high energy resolution X-ray absorption near edge structure (HR-XANES) spectra contain additional information compared to the conventional XANES spectra, as they are rich in resolved resonant spectral features for specific An oxidation states.[1]The An $M_{4,5}$ edge HR-XANES probes directly the An valence unoccupied 5f states (3d→5f) and thus yields insight to the role these frontier orbitals play in hybridization with ligands and bond formation.

The characterization capabilities of the An $M_{4,5}$ and L_3 edge HR-XANES technique will be highlighted by recent results obtained for both model and complex U, Np and Pu materials. In one example, a single crystal of dicesium uranyl tetrachloride ($Cs_2UO_2Cl_4$) as a model UO_2^{2+} (uranyl ion) compound was investigated using U M_4 ($3d_{3/2} \rightarrow 5f$) and L_3 ($2p_{3/2} \rightarrow 5f/6d$) edge polarization dependent HR-XANES (PD-HR-XANES) with remarkable energy resolution. Comparison of experimentally determined relative energies of U $5f\delta$, $5f\phi$, $5f\pi$, and $5f\sigma$ orbitals, as well as 5f and 6d orbitals obtained from the spectra, to predictions from quantum chemical Amsterdam density functional theory (ADF) and FEFF codes and show excellent results.[2] A number of examples for determination of An redox states in liquids and solid systems will be discussed. Comparison of U/Pu/Np M_4/M_5 HR-XANES spectra of UO_2^{2+}, NO_2^{2+} and PuO_2^{2+} as well as Pu M_5 HR-XANES and L_3 XANES of various Pu oxidation states in aqueous solution will be presented. In addition, recent results unambiguously demonstrate that U(V) can exist alongside U(IV) and U(VI) in magnetite nanoparticles under anoxic conditions; this underpins the utility of HR-XANES for understanding U retention mechanisms on corrosion products.

[1] At. Vitova, M. A. Denecke, J. Göttlicher, K. Jorissen, J. J. Kas, K. Kvashnina, T. Prüßmann, J. J. Rehr, J. Rothe, Journal of Physics: Conference Series , 430; Bk. O. Kvashnina, S. M. Butorin, P. Martin, P. Glatzel, Phys Rev Lett , 111; Ct. Vitova, K. O. Kvashnina, G. Nocton, G. Sukharina, M. A. Denecke, S. M. Butorin, M. Mazzanti, R. Caciuffo, A. Soldatov, T. Behrends, H. Geckeis, Phys Rev B , 82.

[2] T. Vitova, J. C. Green, R. G. Denning, M. Löble, K. Kvashnina, J. J. Kas, K. Jorissen, J. J. Rehr, T. Malcherek, M. A. Denecke, Inorganic Chemistry , 54, 174-182.

3:00pm **AC+AS+MI-WeA3 Soft X-ray Spectromicroscopy of Actinide Materials**, ***David Shuh***, Lawrence Berkeley National Laboratory **INVITED**

Soft X-ray synchrotron radiation methodologies are being developed and employed at the Advanced Light Source (ALS) of Lawrence Berkeley National Laboratory to elucidate the electronic structure of actinide materials. Results from these investigations have begun to provide improved fundamental knowledge that can be used as a scientific basis for the enhanced design of special-purpose actinide materials and the overall understanding of actinide materials. The experimental developments at the ALS have centered on the use of the Molecular Environmental Science (MES) scanning transmission X-ray microscope (STXM) at Beamline 11.0.2 for near-edge X-ray absorption spectroscopy (XAS), and on X-ray emission spectroscopy (XES) at several beamlines, focusing primarily on light atom constituents (C, N, O, F) for ligand K-edge XAS, and on metal-ion centers plus light-atom signals for XES. The spectromicroscopy capabilities of the STXM provide the means to investigate and determine the speciation in actinide materials and environmentally-relevant systems with spatial resolution that reaches to the true nanoscale.

An absolutely critical and key enabling component for all of the soft X-ray investigations is the contribution of theory, that when combined with experiment, has firmly provided more detailed knowledge of electronic structure in actinide materials in terms of orbital composition and mixing, and oxidation state. The highlights of recent investigations of metallocenes at the carbon K-edge and uranyl complexes at the nitrogen K-edge will be highlighted in this respect. The spectromicroscopy attributes of the STXM have enabled the investigation of contaminant speciation in a range of model and real environmental systems. The results of the most recent environmentally-related studies, cesium in clay materials relevant to clean up efforts in Japan, will be presented.

Acknowledgement: Supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences Heavy Element Chemistry Program of the U.S. DOE at LBNL under Contract No. DE-AC02-05CH11231.

4:20pm **AC+AS+MI-WeA7 Resonant Ultrasound Spectroscopy Detects 100 Part-per-billion Effects in Plutonium**, ***Albert Migliori***, Los Alamos National Laboratory **INVITED**

The speeds of sound, or, equivalently, the elastic moduli are some of the most fundamental attributes of a solid, connecting to fundamental physics, metallurgy, non-destructive testing, and more. With modern advances in electronics and analysis, changes in elastic moduli are detectable at 100 parts per billion, providing new and important insight into grand challenges in plutonium science. Applied to ^{239}Pu, the effects of aging are measured in real time as a function of temperature, and the temperature dependence of the elastic moduli of gallium stabilized delta plutonium leads to important questions about the validity of electronic structure theory, and points towards inescapable constraints on any theory of this metal.

This work was supported as part of the Materials Science of Actinides, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award # DE-SC0001089.

5:00pm **AC+AS+MI-WeA9 Spectroscopic Studies of the Oxide Layer formed on Plutonium under Ambient Conditions**, ***Alison Pugmire***, Los Alamos National Laboratory, *C.H. Booth*, Lawrence Berkeley National Laboratory, *J. Venhaus, L. Pugmire*, Los Alamos National Laboratory

One of the fundamental challenges of modern science lies in understanding the chemistry and physics of the actinides, and in particular, plutonium. It's unpredictable behavior and reactivity has led to a very poor understanding of its metallurgy and corrosion process. This not only poses a basic scientific challenge, but directly affects the safe, long term storage of this material. In an effort to understand the surface chemistry and corrosion of plutonium, knowledge of the surface oxide composition is paramount. The currently accepted description of the oxide layer formed under ambient temperatures and pressures consists of a thick PuO_2 surface layer over a thin Pu_2O_3 layer at the metal interface. However, recent studies by our group indicate this description is inadequate, and the oxide layer formed in the initial stages, in particular, is much more complex. We have recently focused on studying the oxide layer formed on gallium stabilized δ-plutonium in ambient conditions (pressure, temperature). We have characterized this layer using multiple spectroscopic techniques, including spectroscopic ellipsometery (SE), x-ray photoelectron spectrosocopy (XPS), and x-ray absorption spectroscopy (XAS). This diverse and complimentary suite of experimental techniques will address many long-standing issues regarding the nature of the oxide layer and the corrosion mechanism.

5:20pm **AC+AS+MI-WeA10 Covalent Mixing In Actinide and Lanthanide Compounds: Reliable Assignment of Cation Charges**, ***Paul Bagus***, University of North Texas, *C.J. Nelin*, Consultant

The importance of covalent and ionic interaction and bonding in heavy metal oxides, for example for the actinide dioxides, AnO_2, is controversial with some claiming that the interactions are nearly purely ionic and with others arguing that there is important covalent character. Similar questions also exist for halides and for lanthanide compounds. One way to view this is to consider how close the actual charge state of the cation is to the nominal oxidation state. Our analysis is based on using wavefunctions for embedded clusters which model the bulk oxides. With these wavefunctions, we show that considerable departures of the cation charge from the nominal value are a common occurrence. We also show how the departure from the nominal charge state depends on several factors including: (1) nominal oxidation state, (2) ligand, and (3) position in the row of the periodic table. It is also necessary to determine which metal orbitals are involved in the covalent mixing. For actinides, the natural choice is the open cation 5f shell but the normally empty 6d shell may also contribute to the covalent mixing and, in fact, may even have a larger contribution than the 5f. In order to characterize the extent and importance of the covalent mixing, two factors need to be taken into account: (1) the estimate of the actual charge state of the cations and (2), perhaps even more important, the contribution of the covalent mixing of the cation and anion frontier orbitals to the total energy of the compound. Our approach to address both of these aspects is to limit the variational freedom when we self-consistently optimize the orbitals of the models used to represent the compounds studied. By restricting the variational space, the importance of the mixing of ligand and metal frontier orbitals can be explicitly measured by determining the difference between a wavefunction where these frontier orbitals are excluded from the variational process and a wavefunction where they are allowed to mix with other orbitals. With this approach, it is possible to make quantitative estimates of energies associated with the covalent mixing as well as the effective charges that can be associated with the cations and ligands. Furthermore, it is possible to visualize the changes in the charge distribution for different degrees of variational freedom with suitable contour plots. We acknowledge support for this work by the Geosciences Research Program, Office of Basic Energy Sciences, U.S. DOE.

5:40pm **AC+AS+MI-WeA11 An XPS and ToF SIMS Investigation of Cerium Oxidation**, ***Paul Roussel***, AWE, United Kingdom of Great Britain and Northern Ireland

In this study fcc γ-cerium has been used as a non radioactive surrogate material for fcc δ-plutonium. The common cerium oxides are the trivalent sesquioxide and the tetravalent dioxide both of which are iso-structural with the oxides formed on plutonium metal. Similarly, cerium (1) like plutonium (2) dsiplays parabolic oxidation kinetics at low temperatures and linear kinetics elevated temperatures. This makes cerium an ideal surrogate material to study the kinetics and mechansim of plutonium oxidation. The initial oxidation of cerium at 274 K was studied using X-ray Photoelectron Spectroscopy. On exposure to Langmuir quantities of oxygen cerium rapidly oxidizes to to the trivalent oxide followed by the slower growth of the tetravalent oxide. The growth modes of both oxides have been determined. It was found the surface formed tetravalent oxide was unstable in ultra high vacuum and reduced to the trivalent oxide by an apparent solid state diffusion reaction with cerium metal. This reduction reaction can be explained by the thermodynamic unstability of the tetravalent dioxide with respect to cerium metal. The complexity of this reduction reaction appears to be enhanced by the formation of surface hydroxyl species as a function of time. Time of Flight Secondary Ion Mass Spectrometry was used to support characterization of the surface hydroxyl species.

(1) D. Cubicciotti, J. Am. Chem. Soc., 74 (1952) 1200.

(2) J. L. Stakebake, J. Less Common Met., 123 (1986) 185.

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Applied Surface Science
Room: 212D - Session AS+SS-WeA

Characterization of Buried Interfaces
Moderator: Xia Dong, Eli Lilly and Company, James Ohlhausen, Sandia National Laboratories

2:20pm **AS+SS-WeA1 ASSD 30th Anniversary Speaker: Characterization of Sub-surface Interfaces using SIMS, TEM, and FIB or: How Much will it Cost me to Fix that Interface?**, ***Fred Stevie***, North Carolina State University **INVITED**

Characterization of interfaces between layers or between layer and substrate has always been of interest. Interface issues include visible problems, such as delamination or corrosion, and contamination that can affect product quality, such as electrical properties in semiconductors. The information desired includes the physical quality of the interface and identification and quantification of contaminants. This presentation summarizes multiple approaches to interface analysis, particularly with use of SIMS, FIB, and TEM.

Common approaches for analysis of a buried interface involve a depth profile or cross section. Depth profiling by SIMS is often used because of good sensitivity and depth resolution. Matrix, dopant and contaminant species in the structure can be characterized with a single SIMS depth profile. Quantification of contamination at an interface is highly desired but can be difficult to obtain. Once an element has been identified as a contaminant, quantification at interfaces may be possible with ion implantation. Significant improvements have been made with the species used for depth profiling. C_{60} and argon cluster beams are used to depth profile organic materials. These high mass ion beams provide better sensitivity for high mass species and do not affect the chemical composition, so it is possible to obtain interfacial chemistry.

The FIB has revolutionized sample preparation and lift-out methods can routinely prepare cross section specimens for TEM analysis. A sample polished to provide an edge can rapidly be trimmed with FIB to provide a surface 50 to 100µm in height that is suitable for high resolution analysis. Optimization of beam conditions such as dwell and overlap can increase removal rate by several times. Plasma ion sources dramatically increase material removal rates and make possible the study of 100µm deep interfaces which will cover most layers of interest. Plating coatings are commonly less than 5µm thick and paint coatings 100 to 150µm.

3:00pm **AS+SS-WeA3 FIB-TOF Tomography Characterization of Organic Structures**, ***David Carr***, *G.L. Fisher,* Physical Electronics USA, *S. Iida, T. Miyayama*, ULVAC-PHI

1. Introduction

There are practical limitations to the use of ion beam sputtering for probing the sample chemistry beyond the surface region which include preferential sputtering and accumulated sputter beam damage. Both effects result in a distortion or complete loss of the true 3D chemical distribution as a function of depth

An alternative approach to achieve 3D chemical imaging of complex matrix chemistries is to utilize *in situ* FIB milling and sectioning in conjunction with TOF-SIMS chemical imaging, or 3D FIB-TOF tomography [1]. This can minimize or eliminate artifacts caused by sputter depth profiling such as differential sputtering and accumulated ion beam damage.

However, even with FIB polishing there remains some FIB beam-induced chemical or molecular damage that may or may not limit the detection of characteristic molecular signals. For certain specimens, it is an advantage to follow FIB polishing with cluster ion polishing to recover the characteristic molecular signals.

2. Method

The 3D chemical characterization of pure organic and metal-organic mixed composition structures was achieved utilizing 3D FIB-TOF tomography on a PHI TRIFT *nanoTOF* II (Physical Electronics, USA) imaging mass spectrometer. The spectrometer's large angular acceptance and depth-of-field maintain high mass resolution and high mass scale linearity even in this challenging geometry. This provides the highly desirable ability to perform artifact-free chemical imaging of high aspect ratio features.

3. Results

The present study investigated samples from two classes of materials: one metal-organic mixed matrix composition and one mixed organic phase comprised of two polymer moieties. Since there was no preferential sputtering, an immediate result of the FIB-TOF imaging was the accurate determination of the depth scale. We have collected characteristic molecular information from each sample for the purposes of 2D and 3D imaging. Cluster ion beam polishing (e.g. C_{60}^+ or $Ar_{2,500}^+$) was necessary to remove the FIB beam-induced damage, and the new instrument configuration allows cluster ion polishing to be accomplished with ease. We will highlight certain aspects of the studies for presentation.

4. References

[1] A. Wucher, G.L. Fisher and C.M. Mahoney, Three-Dimensional Imaging with Cluster Ion Beams (p. 207-246) in *Cluster Secondary Ion Mass Spectrometry: Principles and Applications*, C.M. Mahoney (Ed.), Wiley & Sons, N.J. (2013).

4:20pm **AS+SS-WeA7 Interface Characterization using Ballistic Electron Emission Microscopy and Spectroscopy: Recent Results and Related Techniques**, ***Douglas Bell***, Jet Propulsion Laboratory, California Institute of Technology **INVITED**

Ballistic electron emission microscopy (BEEM) is a microscopy and spectroscopy based on scanning tunneling microscopy (STM), developed as a scanning probe of subsurface interface properties. By monitoring the fraction of tunneling current between STM tip and sample that traverses a subsurface heterostructure, BEEM can probe hot-carrier transport as well as heterostructure and material properties. Because BEEM uses an STM tip to inject a highly localized carrier distribution, high-resolution imaging of interface electronic structure can be performed. Control of tunnel voltage polarity allows injection of either holes or electrons into the sample structure, thus enabling characterization of electronic structure both above and below the Fermi level.

Since its inception, BEEM has found many applications such as studies of interface heterogeneity, carrier scattering, band structure, transport in oxides, and interface chemistry. A wide range of structures have been probed, including metal/semiconductor, metal/oxide/semiconductor, quantum wells, and quantum dots. Researchers have measured quantized energy levels and spatial variations of Schottky barrier height. BEEM has also provided a new means for studying fundamental characteristics of interface transport such as conservation of momentum parallel to an interface.

More recently, BEEM has been applied to the investigation of other novel materials and structures. Organic materials, graphene layers, and nanowires have received attention, and research has been done on molecular vibrational spectroscopy. Related techniques for magnetic materials, and measurements of BEEM-induced luminescence, have been further developed and demonstrated.

This talk will discuss some of these recent advances and extensions, as well as further developments in more traditional areas. Some comparisons with results from other characterization techniques will also be presented.

5:00pm **AS+SS-WeA9 Using XPS to Study Electrochemical Solid-Liquid Interfaces In-Operando: Standing-Wave Ambient-Pressure XPS (SWAPPS)**, ***Osman Karslioglu***, Lawrence Berkeley National Laboratory, *S. Nemsak*, Forschungszentrum Juelich GmbH, Germany, *I. Zegkinoglou, A. Shavorskiy, M. Hartl, C.S. Fadley, H. Bluhm*, Lawrence Berkeley National Laboratory

Accessing the chemical and electrical potential information at a solid/liquid interface is an important capability for investigating a process like corrosion where electrochemical transformations are at work. Here we report the first results of a combination of techniques, where we use X-ray standing waves to enhance the photoemission signal from the solid-liquid interface during an ambient-pressure XPS experiment, investigating the oxidation of Ni. X-ray standing waves were generated by a Si/Mo multilayer mirror, on which the sample is prepared as a thin layer (~8 nm Ni in this case). A thin liquid layer was formed on the surface by dipping the sample into an electrolyte (KOH(aq), 0.1 mol/L) and pulling back partially. The solid-liquid interface was probed through this thin liquid layer using hard X-rays (3100 eV). The sample was the working electrode in a 3-electrode cell, and it was oxidized by applying a positive potential using the potentiostat. Comparing the experimental rocking curves for Ni 3p and O 1s with theory provided thickness and roughness information for solid and liquid layers with ~1 nm resolution.

5:20pm **AS+SS-WeA10 Exploring the Usefulness of Monochromatic Ag Lα X-rays for XPS**, ***Sarah Coultas***, *J.D.P. Counsell, S.J. Hutton, A.J. Roberts, C.J. Blomfield*, Kratos Analytical Limited, UK

High energy X-ray sources have been used in XPS analysis for some time to access more core-levels and probe deeper into the sample surface. Lab based sources such as Zr and Ti have been offered in the past but the broad X-ray line widths produced by such sources limit their applications for chemical analysis. This problem is mitigated by the use of an Ag Lα X-ray source. The source energy is 2984 eV, conveniently approximately twice that of Al Kα, hence the same quartz crystal mirror may be used to monochromate the Ag Lα X-ray line producing a narrow, high energy source of X-rays for XPS. Modern X-ray photoelectron spectrometers may be fitted with automated Al / Ag X-ray monochromators which greatly improve the usability of Ag Lα X-rays allowing Al and Ag X-ray generated spectra to be recorded from the same sample as part of automated data acquisition. Highlights of the source's characteristics include:

- Good sensitivity and energy resolution provide useful chemical information
- Enhanced surface compositional information from approximately twice the analytical depth as Al Kα radiation for same core line
- Higher excitation energy allows deeper core levels and additional Auger lines to be explored
- Large energy range of Ag Lα allows exploitation of "depth dimension" for surface segregation studies

Here we investigate the practical uses of these characteristics. This includes using the Auger parameter for aluminium and silicon containing compounds where the higher energy radiation can excite the 1s core lines and the KLL Auger series. Earlier studies [1] have shown the usefulness of higher excitation energies in elucidating structure via Auger parameters.

We also illustrate the usefulness of Ag Lα as an additional tool for the surface analyst by way of examples of spectroscopy, ARXPS, depth profiling and imaging.

1. References

[1] J.E. Castle, L.B. Hazell & RH West, *J. Electron Spectrosc. Relat. Phenom.* ., 1979, **16**, 97

5:40pm **AS+SS-WeA11 Optimizing the TOF-SIMS CsM^+ Depth Profile of a Tunnel Magneto Resistance (TMR) Structure**, ***Alan Spool***, HGST, a Western Digital Company

Used now for many years in modern magnetic recording devices, TMR sensors consist at their heart of a complicated series of layers, mostly metallic, ranging in thickness from less than a nm to several nm. In order to use the potentially better depth resolution and sensitivity of a SIMS depth profile over other surface analytical techniques, CsM^+ profiles were obtained using a variety of conditions. The ratio of the sputter ion to primary ion fluences, the sputter ion beam energy, and the % of Cs in a combined Cs/Xe sputter ion beam were all varied, and the results for a single wafer compared. In addition to changes in various CsM^+ ion intensities and therefore their signal to noise, the Cs/Xe ratio sometimes had unexpected effects on the profile shapes. The primary ion beam fluence was lessened by increasing its raster size over more than the crater bottom. Depth profiles were then created retrospectively from the raw data, using the results themselves to select the flattest portion of the crater bottom.

6:00pm **AS+SS-WeA12 Interface and Composition Analyses versus Performances: How to Improve Perovskite Solar Cells**, *Y. Busby*, University of Namur, B-5000 Namur, Belgium, *F. Matteocci,* University of Rome "Tor Vergata", Italy, *G. Divitini, S. Cacovich,* University of Cambridge, UK, *C. Ducati,* University of Cambridge, *A. di Carlo,* University of Rome "Tor Vergata", Italy, ***Jean-Jacques Pireaux***, University of Namur, Belgium

Hybrid halide perovskite solar cells (PSCs) have received much attention during the very last years because of their very promising cost/performance ratio. Different architectures and preparation methods have been tested, but still some general guidelines for their optimization are missing. In particular, the interfaces are now well known to play a dominant role in the device performances but have been so far poorly studied.

In this work, we correlated the solar cell characteristics to their interface composition and morphology in PSCs deposited by different procedures (single-step, double-step by dipping, double-step by a vacuum assisted technique) and different conversion environments (air, vacuum and nitrogen atmosphere). The interface quality is found to be affected by the perovskite conversion method and in particular from the environment where the conversion is performed. Power conversion efficiencies between 7 and 14.5% have been measured from the characteristics of the differently prepared cells. The morphology, crystal size and interdiffusion have been fully characterized by scanning transmission electron microscopy (STEM), equipped with high resolution energy-dispersive X-ray spectroscopy (EDX). Interfaces have been further characterized by depth profile techniques by combining ion beam sputtering with atomic and molecular composition analysis with X-Ray photoelectron spectroscopy (XPS) and Time of Flight Secondary Ion Mass Spectroscopy (ToF-SIMS). In particular these techniques allowed detecting and evaluating the diffusion of metals into the hole transport material (SpiroOMetAD) and iodine and chlorine diffusion in the TiO_2 back contact. Interestingly, the higher oxygen content perovskite formed in air is not associated to a sensibly lower (short term) efficiency of the solar cell.

Biomaterial Interfaces
Room: 211D - Session BI-WeA

Biophysics, Membranes and Nanoscale Biological Interfaces
Moderator: Stephanie Allen, The University of Nottingham, UK

2:20pm **BI-WeA1 Direct Measurement of Single Molecule Interaction Free Energies at Solid/Liquid Interfaces for the Prediction of Macroscopic Properties**, ***Markus Valtiner***, *S. Raman, T. Utzig, P. Stock*, Max Planck Institut fur Eisenforschung GmbH, Germany

Unraveling the complexity of the macroscopic world based on molecular level details relies on understanding the scaling of single molecule interactions towards integral interactions at the meso- and macroscopic scale. Here, we discuss how one can decipher the scaling of individual single binding interactions at solid/liquid interactions towards the macroscopic level [1], where a large number of these bonds interacts simultaneously. We developed a synergistic experimental approach combining Surface Forces Apparatus (SFA) experiments and single molecule force spectroscopy (SMFS). We show that equilibrium SFA measurements scale linearly with the number density of a model acid-base bond at an interface, providing acid-amine interaction energies of 10.9 ± 0.2 kT. Using Bell-Evans theory together with Jarzynski's equality, we can demonstrate how a set of single molecule interaction forces measured by SMFS similarly converges to an interaction energy of 11 ± 1 kT, with unbinding energy barriers of 25 kT ± 5 kT. This indicates excellent predictive power of our newly developed scaling approach.

In addition, we tested a number of other bonds including hydrophobic, ligand-receptor and metal-polymer bonds with our model and find that our model is widely applicable. Hence, we will discuss in detail how single molecule unbinding energy landscapes can be utilized to predict scenarios where a large number of molecules simultaneously interact, giving rise to both macroscopic equilibrated and non-equilibrated interaction energies during adhesive failure. As such, our experimental strategy provides a unique framework for molecular design of novel functional materials through predicting of large-scale properties such as adhesion, self-assembly or cell-substrate interactions based on single molecule energy landscapes.

[1] S. Raman et al. *inNature Communications***,** 5**(2014)**, 5539.

[2] T. Utzig et al. *in Langmuir*, 31(9) **(2015)**, 2722.

2:40pm **BI-WeA2 Multipurpose Biomembranes of Sandwiches Layers: Deposition and Characterization with Surface and Biological Methods***,* *H. Heidari Zare,* Munich University of Applied Sciences, Germany*, D. Jocham,* University Hospital of Schleswig-Holstein, Germany*, **Gerhard Franz***, Munich University of Applied Sciences, Germany

For coating of medical implants, two different strategies have been evolved, either films which can be decomposed after a certain time of impact, or "eternal" layers. Both types can be composed as a homogeneous film or a heterogeneous sandwich layer, which have the charm that the same coating layer can be used not only to protect different pharmaceutical depot layers on top of different substrates but also to allow a retarded emission of drugs, which can be adjusted by its porosity. Our coatings are made of FDA-passed poly-(p-xylylene), or parylene, PPX. It is employed it two systems: for coronary stents, or in antibacterial urinary catheters. In the first case, it protects a restenotic drug which is applied on top of a plasma-roughened metallic surface, in the second application, the porous cap layer protects a silver film, which is deposited on the interior walls of a catheter in a random zebra-stripe design without application of a mask technology. Its morphology can be adjusted by the conditions of preparation.

For capillaries, one challenge is the homogeneous thickness on the interior sidewall from the mouth to the dead end of the capillary, which has been solved by application of a temperature seesaw: Since condensation is an exothermic process, application of the principle of Le Chatelier moves the equilibrium of diffusion with deposition loss to the side with higher internal energy, i. e. to the vaporous phase, thereby equalizing the deposition rate, downward at the mouth and upward at the dead end.

The porosity of the cap layer can be adjusted by its thickness between zero and approx. 1000 nm [1]. Especially for the Gorham method, which is widely applied for the deposition of PPX, thicknesses below 1 μm are difficult to obtain. Applying a method which resembles Papin's principle, this challenge could also be met [2].

The porosity is judged by atomic force microscopy (AFM) and electrochemical impedance spectroscopy (EIS), the loss rate by ICP-OES and polarography, the medical impact by measuring the optical density and applying a growth inhibition test [3]. One of the medical challenges is the confirmation of the minimum inhibition concentration of these compound layers.

[1] F. Schamberger, A. Ziegler, and G. Franz, J. Vac. Sci. Technol. B 30, 051801 (2012)

[2] G. Franz and F. Schamberger,. J. Vac. Sci. Technol. A 31, 061602 (2013)

[3] H. Heidari Zare, St. Sudhop, F. Schamberger, and G. Franz, Biointerphases 9, 031002 (2014)

3:00pm **BI-WeA3 Vascularized Micro-Tissue Engineered Constructs for Drug Screening***, **Noo Li Jeon***, Seoul National University, Korea **INVITED**

Vasculature is a fundamental building block of tissues. In order to design and fabricate in-vitro organ-on-chip systems, vasculature needs to be integrated with the micro-tissue constructs.

This presentation will describe the development of a novel microfluidic device with perfusable network of blood vessels that: 1) reproduce angiogenesis and vasculogenesis, 2) allow formation of network of perfusable endothelial vessels in 3D tissue, 3) allow observation of cancer and immune cell intravasation and extravasation, and 3) allow measurement of microvessel permeability. Cancer cells can be introduced and their intravasation and extravasation can be observed with live-cell imaging for extended periods and thus control the tumor microenvironment for investing different steps of metastatic cascade. Characterization of the vessels with immuno-histochemical techniques show that tight-junctions form between the endothelial cells and laminin and collagen IV are deposited along the length of the vessel.

The development of vascularized micro-tissue represents a step forward in building organ-on-chip systems. Drug screening and other assays can be performed using live-cell imaging and immunohistochemistry techniques enabling high throughput testing of multiple conditions simultaneously.

4:20pm **BI-WeA7 Controlling Cell Adhesion on Device Surfaces by Nanotopography***, **Elena Liang**, E. Mah, S. Wu, A. Yee*, University of California, Irvine

The ability to control cell adhesion on material surfaces is critical to the performance and biointegration of implanted medical devices. Of particular interest to our research is developing an understanding of what role surface topography plays in cell adhesion, which could lead to simple and durable ways to engineer surfaces without having to chemically modify the surface of biomaterials. Our group found that human embryonic stem cells grown on nanopillar structures have a significantly reduced number of focal adhesions per cell and concordantly exhibit increased cell motility on the nanopillars (Kong *et al*. 2013). We hypothesized that pillar nanostructures would prevent cells from adhering. To test this hypothesis, we counted the number of fibroblasts adhering to a variety of surface topographies, which consisted of a flat surface, nanolines, and nanopillars, and examined cell morphology on these surfaces. We created a library of nanopillared polymethylmethacrylate (PMMA) surfaces, including a biomimetic cicada wing replicate (the surface of the wing has a high density of nanopillars with dimensions that are ideal for our studies) made by compressing a negative hPDMS stamp of the cicada wing into PMMA, and pillar arrays of approximately 200 nm diameter nanopillars with center-to-center spacing ranging from 320 nm to 692 nm fabricated with nanoimprint lithography. We also observed the focal adhesions using fibroblasts transfected with paxillin-GFP and tracked migration. After 24 hours, we found that the fibroblasts showed a spread-like morphology on the flat film while those on pillars were smaller and more equiaxed. Preliminary results show that there are noticeably fewer cells on PMMA pillars than on flat PMMA. The focal adhesions on cells on nanopillars appear smaller than focal adhesions of cells on a flat surface. Lastly, cells on nanopillars on average traveled a greater distance than cells on a flat surface. Our study shows that protruding structures in the 100-500 nm size range affect cell adhesion dynamics and structure dimensions modulate the adhesion of cells. This may provide researchers a useful means of controlling cell adhesion on surfaces of implants.

4:40pm **BI-WeA8 Condensation-Mediated "Living" Chain Growth Polymerization: Towards New DNA Nanostructures**, *L. Tang, R. Gu,* Duke University*, J. Lamas,* Texas State University*, N. Li,* North Carolina State University*, S. Rastogi,* Texas State University*, A. Chilkoti,* Duke University*, W. Brittain,* Texas State University*, Y.G. Yingling,* North Carolina State University*, **Stefan Zauscher***, Duke University

Polynucleotide co-polymers promise a rich micellization behavior in solution and hold promise for novel functional materials in nano- and biotechnological applications. We report on the synthesis of biologically-inspired polynucleotides with well-defined sequence, dispersity, and assembly function that have large potential for applications ranging from delivery vehicles of medical therapeutics, sensing applications, to scaffolds for nanowires. Specifically, we exploit the ability of the DNA polymerase, terminal deoxynucleotidyl transferase (TdT), to polymerize long chains of single strand DNA (ssDNA) and to incorporate unnatural nucleotides with useful functional groups into the growing polynucleotide chain. Furthermore, we demonstrate the reversible micellar aggregation of a DNA-azobenzene conjugate, in which the photoisomerization of the initially apolar *trans*-azobenzene moiety to the polar *cis* isomer causes disassembly of the aggregates. Finally, we show how coarse-grained simulations can be used to describe the conformational characteristics of the engineered ssDNA blocks and their self-assembly into a rich spectrum of biomolecular nanostructures in solution and on surfaces.

5:00pm **BI-WeA9 Simple Routes to All-Polymeric Corrals, Flow-Channels and Traps for Studies of Lipid and Protein Diffusion in Supported Lipid Bilayers**, *A. Johnson, P.M. Chapman, A.M. Alswieleh,* University of Sheffield, UK*, P. Bao,* University of Leeds, UK*, A. Tsargorodska, S.P. Armes,* University of Sheffield, UK*, S.D. Evans,* University of Leeds, UK*, **Graham Leggett***, University of Sheffield, UK

We describe simple routes to the fabrication of corrals, channels, traps and other structures for the fabrication of spatially organized lipid bilayers and membrane proteins. These utilize photochemistry and polymer brushes. In the first approach, UV exposure of films of (chloromethylphenyl)trichlorosilane (CMPTS) causes dehalogenation of the surface creating carboxylic acid groups to create hydrophilic, anionic regions, in which lipid mobilities are observed that are similar to those observed on glass surfaces. In masked regions, the halogen remains intact, and is used to grow poly(oligoethyleneglycol methacrylate) (POEGMA) brushes by atom-transfer radical polymerization (ATRP), defining lipid-free walls within which SLBs may be formed by vesicle fusion. Two-component structures are fabricated by using an aminosilane film in which the amine group is protected by a photoremovable nitrophenyl group. Selective exposure, through a mask or using a Lloyd's mirror interferometer, causes patterned deprotection of the film leading to patterned brush growth by

ATRP. Poly(Cysteine methacrylate) (PCysMA) is a new, highly biocompatible, stimulus-responsive zwitterionic polymer that forms thick brushes when grown from surfaces by atom transfer radical polymerization (ATRP). Lipid mobility similar to that observed on glass is observed on PCysMA brushes. Measurements of membrane protein diffusion have been made using ac trap structures. After lithographic definition of corrals, channels and other structures, PCysMA is end-capped and the remainder of the surface deprotected; POEGMA brushes are grown by ATRP, enclosing the PCysMA structures. Using interferometric lithography, arrays of close-packed gold nanostructures may be defined on the substrate. These are strongly coupled to photosynthetic membrane proteins, yielding intense extinction spectra. These gold nanostructures are incorporated into brush corrals and other structures, with polymer brushes grown to the same height as the gold nanostructures, enabling the formation of a continuous SLB with integral plasmonic reporters for membrane protein activity.

5:20pm **BI-WeA10 Measuring Cardiomyocyte Contractions on Silicon Carbide Micromechanical Resonators**, ***Hao Tang***, *H. Jia, P.X.-L. Feng*, Case Western Reserve University

Heart functions are mainly determined by its contractility. Monitoring the contraction curve at single cell level may help attain a deeper understanding of cardiomyocyte contraction process[1], heart failure mechanism[2] and potential methods for drug screening. The contraction frequency, contraction amplitude as well as contraction and relaxation rates of cardiomyocytes all together compose the contraction curve and reflect the health condition of heart tissues.

At the single-cell level, most contractility measurement methods are based on measuring the length change[2] or force change[3] of single cardiomyocyte. Methods based on length change often require massive and fast image processing, therefore, its time resolution is restricted by the capturing and processing speed, and spatial resolution is limited by the diffraction of optical system (typically 0.2um). Methods based on force change require complex readout elements that are compatible with biological environments, which on the other hand results in complex fabrication process.

In this work, we take an initial step to measure the cardiomyocyte contraction in a dynamic mode using SiC micromechanical resonators. As a superior material for bioMEMS platforms, SiC has excellent mechanical, optical, chemical, thermal properties as well as unique biocompatibility[4],[5]. Frequency-shift-based sensing using micromechanical resonators[6],[7] offers possibilities of monitoring mass distribution changes during cardiomyocyte contraction process with high sensitivity. Our dynamic sensing method provides an alternative for cardiomyocyte contraction measurement, with promising applications in heart failure research and drug screening.

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5:40pm **BI-WeA11 Programming the Robust Self-organization of Human Tissues using Interfacial Interactions**, ***Zev Gartner***, University of California, San Francisco **INVITED**

Developing tissues contain motile populations of cells that can self-organize into spatially ordered tissues based on differences in their interfacial surface energies. However, it is unclear how self-organization by this mechanism remains robust when interfacial energies become heterogeneous in either time or space. The ducts and acini of the human mammary gland are prototypical heterogeneous and dynamic tissues comprising two concentrically arranged cell types. To investigate the consequences of cellular heterogeneity and plasticity on cell positioning in the mammary gland, we reconstituted its self- organization from aggregates of primary cells in vitro. We find that self-organization is dominated by the interfacial energy of the tissue–ECM boundary, rather than by differential homo- and heterotypic energies of cell–cell interaction. Surprisingly, interactions with the tissue–ECM boundary are binary, in that only one cell-type interacts appreciably with the boundary. Using mathematical modeling and cell-type-specific knockdown of key regulators of cell–cell cohesion, we show that this strategy of self-organization is robust to severe perturbations affecting cell–cell contact formation. We also find that this mechanism of self-organization is conserved in the human prostate. Therefore, a binary interfacial interaction with the tissue boundary provides a flexible and generalizable strategy for forming and maintaining the structure of tissues that exhibit abundant heterogeneity and plasticity. Our model also predicts that mutations affecting binary cell–ECM interactions are catastrophic and could contribute to loss of tissue architecture in diseases such as breast cancer.

Electronic Materials and Processing
Room: 211C - Session EM+AS+MS+SS-WeA

Surface and Interface Challenges in Wide Bandgap Materials

Moderator: Aubrey Hanbicki, U.S. Naval Research Laboratory, Rachael Myers-Ward, U.S. Naval Research Laboratory

2:20pm **EM+AS+MS+SS-WeA1 Effects of Nitrogen and Antimony Impurities at SiO_2/SiC Interfaces**, ***Patricia Mooney***, Simon Fraser University, Canada **INVITED**

4H-SiC is an attractive material for devices operating at high power and high temperatures because of the large bandgap energy, 3.23 eV, the high critical breakdown field, 2.0 $MVcm^{-1}$, and high electron mobility,

850 $cm^2V^{-1}s^{-1}$. Commercialization of 4H-SiC MOSFET technology was long delayed due to the high density of defects near the SiO_2/SiC interface. Post oxidation annealing in NO ambient, the process that enabled the commercialization of SiC Power ICs in 2011, significantly reduces the density of near-interface traps and results in typical effective MOSFET channel electron mobility (μ_{FE}) values of ~20 $cm^2V^{-1}s^{-1}$ [1]. The relatively high density of near-interface traps having energy levels within 0.5 eV of the SiC conduction band was investigated using constant capacitance transient spectroscopy (CCDLTS). These measurements showed that NO annealing reduced the density of the two near-interface oxide trap distributions, attributed to Si interstitials and substitutional C pairs in SiO_2, by as much as a factor of 10 [1,2].

It has also been shown that introducing impurities such as Na, P, or Sb near the SiO_2/SiC interface further increases μ_{FE}, to peak values of 104 $cm^2V^{-1}s^{-1}$ and to 50 $cm^2V^{-1}s^{-1}$ at high electric field for Sb [3]. The much higher value of μ_{FE} in Sb-implanted MOSFETs was attributed to counter-doping by Sb in SiC near the interface. To investigate the effects of Sb at SiO_2/SiC interfaces, Sb ions were implanted near the surface of the 4H-SiC epitaxial layer and the wafer was annealed at 1550℃ in Ar to activate the Sb donors. Dry thermal oxidation was done at 1150℃ and the sample was then NO-annealed at 1175℃ for 30 or 120 min. CCDLTS results of Sb-implanted MOS capacitors were compared with those having no Sb implant but with similar dry oxidation and NO-annealing processes. The density of near-interface oxide traps was similar in samples with and without Sb, indicating that Sb has little effect on those defects. However, CCDLTS spectra taken at bias and filling pulse conditions that reveal defects in the SiC depletion region, show both the deeper of the two N donor levels at E_C - (0.10±0.01) eV and a second energy level only in Sb-implanted samples at E_C - (0.12±0.01) eV. To our knowledge this is the first measurement of Sb donors in SiC and it confirms counter doping of SiC by Sb near the SiO_2/SiC interface.

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3:00pm **EM+AS+MS+SS-WeA3 Hydrogen Desorption from 6H-SiC (0001) Surfaces**, ***Sean King***, Intel Corporation, *R. Nemanich, R. Davis*, North Carolina State University

Due to the extreme chemical inertness of silicon carbide (SiC), *in-situ* thermal desorption is commonly utilized as a means to remove surface contamination prior to initiating critical semiconductor processing steps such as epitaxy, gate dielectric formation, and contact metallization. *In-situ* thermal desorption and silicon sublimation has also recently become a popular method for epitaxial growth of mono and few layer graphene. Accordingly, numerous thermal desorption experiments of various processed silicon carbide surfaces have been performed, but have ignored the presence of hydrogen which is ubiquitous throughout semiconductor processing. In this regard, we have performed a combined temperature programmed desorption (TPD) and x-ray photoelectron spectroscopy (XPS) investigation of the desorption of molecular hydrogen (H_2) and various other oxygen, carbon, and fluorine related species from *ex-situ* aqueous hydrogen fluoride (HF) and *in-situ* thermal and remote hydrogen plasma cleaned 6H-SiC (0001) surfaces. Using XPS, we observed that temperatures on the order of 700 - 1000°C are needed to fully desorb C-H, C-O and Si-O species from these surfaces. However, using TPD, we observed H_2 desorption at both lower temperatures (200 – 550°C) as well as higher temperatures (> 700°C). The low temperature H_2 desorption was deconvoluted into multiple desorption states that, based on similarities to H_2 desorption from Si (111), were attributed to silicon mono, di, and trihydride surface species as well as hydrogen trapped by sub-surface defects, steps or dopants. The higher temperature H_2 desorption was similarly attributed to H_2 evolved from surface O-H groups at ~ 750°C as well as the liberation of H_2 during Si-O desorption at temperatures > 800°C. These results indicate that while *ex-situ* aqueous HF processed 6H-SiC (0001) surfaces annealed at < 700°C remain terminated by some surface C-O and Si-O bonding, they may still exhibit significant chemical reactivity due to the creation of surface dangling bonds resulting from H_2 desorption due from previously undetected silicon hydride and surface hydroxide species.

3:20pm **EM+AS+MS+SS-WeA4 Chemical and Microstructural Characterization of Interfaces between Metal Contacts and β-Ga_2O_3**, ***Lisa M. Porter***, *Y. Yao, J.A. Rokholt, R.F. Davis,* Carnegie Mellon University*, G.S. Tompa, N.M. Sbrockey, T. Salagaj*, Structured Materials Industries, Inc.

β-Ga_2O_3 is a promising alternative to traditional wide bandgap semiconductors, as it has a wider bandgap (~4.9 eV) and a superior figure-of-merit for power electronics and other devices; moreover, β-Ga_2O_3 bulk single crystals have recently been grown commercially using melt-growth methods. While several groups have demonstrated Ga_2O_3-based devices such as Schottky diodes and MOSFETs, understanding of contacts to this material is limited. In this study, we investigated a variety of metal contacts (Ti, In, Mo, W, Ag, Au, and Sn) to both (-201) β-Ga_2O_3 single crystal substrates (from Tamura Corp.) and β-Ga_2O_3 epitaxial layers grown by MOCVD on various substrates (sapphire and single crystal β-Ga_2O_3) by co-authors at Structured Materials Industries. We have characterized these substrates and epilayers using techniques such as X-ray diffraction and transmission electron microscopy (TEM), which show that the epitaxial layers are oriented (-201) with respect to the substrates. We found that the electrical characteristics of the metal contacts to the Ga_2O_3 epilayers and substrates are highly dependent on the nature of the starting surface and the resulting interface, and less dependent on the work function of the metal than expected. For example, both Ti and bulk In readily form ohmic contacts to Ga_2O_3, whereas other low-workfunction metals, such as Sn, did not form ohmic contacts even after annealing to 800 °C. For Ti ohmic contacts on Sn-doped Ga_2O_3 substrates the optimal annealing temperature was ~400 °C: the electrical characteristics continually degraded for annealing temperatures above ~500 °C. Thermodynamics predicts that Ti will reduce Ga_2O_3 to produce Ti oxide, therefore indicating that the Ti/Ga_2O_3 interface is unstable. In correspondence with this prediction, high-resolution cross-sectional TEM images of 400 °C-annealed samples show the formation of an ultra-thin (~2 nm) interfacial amorphous layer. TEM samples at higher annealing temperature have also been prepared for analysis; electron energy loss spectroscopy will be used to characterize the interfacial composition profiles in these samples to determine the relationship between composition and thickness of the interfacial layer and the electrical degradation of the contacts. Schottky diodes with Au, Mo, W and Sn as the Schottky metal were also fabricated. The Schottky barrier heights (SBHs) showed a weak dependence on the metal workfunction. An overview of the electrical behavior of different metals as ohmic or Schottky contacts to Ga_2O_3 and the interfacial chemistry and microstructure will be presented.

4:20pm **EM+AS+MS+SS-WeA7 Regrown InN Ohmic Contacts by Atomic Layer Epitaxy**, ***Charles Eddy, Jr.,*** U.S. Naval Research Laboratory*, N. Nepal,* Sotera Defense Solutions*, M.J. Tadjer, T.J. Anderson, A.D. Koehler, J.K. Hite, K.D. Hobart*, U.S. Naval Research Laboratory

For the past 25 years, compound semiconductors comprised of elements from group III-B of the periodic table and nitrogen have attracted a sustained, high-level of research focus. More recently they have found growing application to rf and power electronics in the form of advanced transistor structures such as the high electron mobility transistor (HEMT) with and without insulated gates. Key performance parameters for such devices (cut-off frequency for rf transistors and on-resistance for power transistors) are often dominated by the contact resistance. The current best approach to contact resistance minimization involves aggressive processing requirements that challenge device fabrication, especially when insulated gates are required. A potential solution is the regrowth of highly conducting semiconductor contact layers where ohmic contacts are needed. Here we report on initial efforts to employ regrown indium nitride (InN) contact layers by atomic layer epitaxy (ALE) as a low temperature solution to the ohmic contact challenge for III-N transistors. Recently, we have reported that good crystalline quality InN can be grown at less than 250°C by ALE [1]. Here we employ such conditions to grow very thin layers and assess them morphologically and electrically.

InN regrown contact layers of 5nm thickness grown on sapphire are very smooth (rms roughness < 0.17nm) and possess sheet resistances as low at 3.6 kΩ/sq, corresponding to electron sheet carrier densities of 2-3 $x10^{13}$ cm^{-2} and mobilities of 50 cm^2/V-s. These electron mobilities are higher than previously reported (30 cm^2/V-s) for much thicker films (1.3 μm) [2]. Similarly grown 22.5 nm thick InN layers on highly resistive silicon were processed with mesa isolation regions and 20/200 nm thick titanium/gold contact metals. Without any contact annealing, an ohmic contact resistance of $9.7x10^{-7}$ Ω-cm^2 (1.2 Ω-mm) was measured, comparable to the best high temperature alloyed contact to an AlGaN/GaN HEMT.

In our initial non-alloyed ohmic contact process, contact regions were recessed down to the GaN buffer layer to establish physical contact between the highly-conductive InN layer and electrons in the HEMT channel. A 25 nm thick InN layer was then grown by ALE, and the InN-filled ohmic regions were then capped with a Ti/Al/Ti/Au layers. Using the metals as an etch mask, the InN outside of the ohmic regions was etched away. We will report on initial results of application of ALE InN regrown contact layers and the modified fabrication approaches to AlGaN/GaN HEMTs.

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4:40pm **EM+AS+MS+SS-WeA8 High-Temperature Characteristics of Ti/Al/Pt/Au Contacts to GaN at 600°C in Air**, ***Minmin Hou***, *D.G. Senesky*, Stanford University

The high-temperature characteristics (at 600°C) of Ti/Al/Pt/Au contacts to gallium nitride (GaN) in air are reported. GaN is a wide bandgap semiconductor material being developed for high-temperature electronics and micro-scale sensors. Ti/Al/Pt/Au metallization is frequently used for forming ohmic contacts to GaN. However, few studies have been devoted to studying the electrical characteristics of the Ti/Al/Pt/Au metallization at elevated temperatures and even fewer in oxidizing environments. It is not practical to obtain a hermetic sealing at elevated temperatures and a number of sensing applications may require non-hermetic packages. Therefore, the electrical characteristics of Ti/Al/Pt/Au contacts in a hot oxidizing ambient instead of an inert ambient or vacuum can provide new insights. In this work, the electrical and microstructural properties of Ti/Al/Pt/Au contacts to GaN upon exposure to 600°C in air are presented.

In this work, microfabricated circular-transfer-line-method (CTLM) patterns were used as the primary test structure. Ti/Al/Pt/Au were patterned through a standard lift-off process on unintentionally-doped GaN epitaxial layer grown by metal organic chemical vapor deposition (MOCVD) on sapphire. After lift-off, the samples were subject to a rapid thermal annealing (RTA) process at 850°C for 35 seconds in a nitrogen ambient.

To observe the impact of thermal exposure on the electrical and microstructural properties, the test structures were subject to a 10-hour thermal storage test in a furnace (air ambient), during which time the test structures were taken out of the furnace every two hours and their I-V characteristics were measured at room temperature. After the initial 2-hour "burn-in" period, the contact resistance remained stable over the entire reminder thermal storage test, with the variance within less than 3% and the specific contact resistivity remained on the order of 10^-5 Ω-cm^2.

In addition, the samples were subject to in-situ high-temperature I-V tests at 600°C in air both before and after the thermal storage using a high-temperature probe station. The linear I-V response confirms that the contacts remained ohmic after the thermal storage. The contact resistance at 600°C showed minimal change (approximately 9%) for a 20-μm-wide gap CTLM test structure, before and after thermal storage.

The microstructural analysis with atomic force microscopy (AFM) showed minimal changes (less than 0.1%) in surface roughness after thermal storage. The results support the use of Ti/Al/Pt/Au metallization for GaN-based sensors and electronic devices that will operate within a high-temperature and oxidizing ambient.

5:00pm **EM+AS+MS+SS-WeA9 Schottky Contacts and Dielectrics in GaN HEMTs for Millimeter-Wavelength Power Amplifiers**, ***Brian Downey***, Naval Research Laboratory **INVITED**

Although GaN RF transistor technology has begun to enter commercial markets, there are still several active research efforts aimed at extending the operating frequency of GaN devices to the millimeter-wavelength (MMW) frequency range of 30 – 300 GHz. In order to facilitate power gain at MMW frequencies, both geometric device scaling and novel heterostructure/device design are required, which present interesting materials and processing challenges. In this talk, an overview of NRL's approaches to MMW GaN high-electron-mobility transistor (HEMT) technology will be presented. In one approach, N-polar GaN inverted HEMT structures are employed, which places the GaN channel at the surface of the device. In this case, Schottky gate contacts are made directly to the N-polar GaN channel. The effect of GaN crystal polarity on Schottky barrier height will discussed along with strategies to increase the Schottky barrier height of metals to N-polar GaN. In a second approach, Ga-polar GaN HEMTs with vertically-scaled barrier layers are utilized to reduce the surface-to-channel distance in order to maintain electrostatic control of the channel in short gate length devices. The high electric fields in these vertically-scaled barrier devices can create large tunneling-related gate leakage currents, leading to high off-state power dissipation and soft breakdown characteristics. The use of gate dielectrics in these scaled structures will be discussed including their effect on device electrical performance.

5:40pm **EM+AS+MS+SS-WeA11 Nitrogen as a Source of Negative Fixed Charge for Enhancement Mode Al2O3/GaN Device Operation**, ***MuhammadAdi Negara***, *R. Long, D. Zhernokletov, P.C. McIntyre*, Stanford University

In recent years, significant research efforts have focused on developing enhancement mode (E-mode) GaN-based devices fueled by many potential applications. Simpler power amplifier circuits using a single polarity voltage supply and increased safety using a normally-off device can be achieved using E-mode devices leading to lower cost and an improvement of system reliability. Using the combination of E-mode and depletion mode (D-mode) devices in direct coupled logic open up also new applications for nitride semiconductors. To realize normally-off operation of GaN transistors, several approaches have been reported in the past including recessed gate structures [1], p-type gate injection [2], fluorine plasma treatment [3], surface channel GaN [4], thermally oxidized gate insulator [5] and oxide charge engineering [6]. In this report, nitrogen impurities introduced during atomic layer deposition of an Al$_2$O$_3$ gate dielectric are investigated as a means of modifying the threshold voltage (V$_{th}$)/flat band voltage (V$_{fb}$) of GaN MOS devices. As reported in reference [7], nitrogen may incorporate on either cation or anion substitutional sites or on interstitial sites in Al$_2$O$_3$ and become a source of negative fixed charge within Al$_2$O$_3$. The effectiveness of this approach for fixed charge modification of ALD-grown Al$_2$O$_3$ compared to several alternative approaches will be presented.

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6:00pm **EM+AS+MS+SS-WeA12 Activation of Mg-Implanted GaN Facilitated by an Optimized Capping Structure**, ***Jordan Greenlee***, *B.N. Feigelson, T.J. Anderson, K.D. Hobart, F.J. Kub*, Naval Research Laboratory

For a broad range of devices, the activation of p and n-type implanted dopants in GaN is needed. The activation of implanted ions by annealing requires post-implantation damage removal and the arrangement of implanted ions in their proper lattice sites. Post-implantation activation of Mg via annealing requires high temperatures (>1300 °C). At these high annealing temperatures, GaN decomposes, leaving behind a roughened surface morphology and a defective crystalline lattice, both of which are detrimental for GaN device applications. To combat decomposition, either a high pressure environment, which is prohibitively expensive and not easily scalable, or a capping structure combined with short exposure to T >1300°C is required to preserve the GaN. In this work, we explore the effects of different capping structures and their ability to protect the GaN surface during a high temperature pulse, similar to those used in the Multicycle Rapid Thermal Annealing (MRTA) process.

It was determined that the sputtered cap provides sufficient protection for the underlying GaN during a rapid heat pulse. The in situ MOCVD-grown AlN cap, although it should have a better interface and thus provide more protection for the GaN layer, is inferior to the sputtered cap as determined by Nomarski images. After etching the surface with AZ400k developer, it was determined that the GaN underneath the MOCVD-grown cap has pits as-grown. Since both GaN layers were grown with the same recipe, we attribute these pits to the HT MOCVD AlN growth process. Atomic force microscopy was used to determine the as-grown and post annealing surface morphologies of the samples. The as-grown sample covered with MOCVD AlN does not exhibit the same smooth step flow growth as the as-grown sample without the MOCVD AlN cap. After annealing and etching off the AlN caps, the surface that was capped with MOCVD AlN shows evidence of pitting while the sample that was protected with only sputtered AlN no longer exhibits step flow growth like the as-grown sample. Since we are above 2/3 of the melting point of GaN, we expect that bulk diffusion is occurring and causing this rearrangement at the surface. This implies that sputtered AlN can provide sufficient protection of the underlying GaN surface, which will facilitate mid-process implantation and activation of Mg in GaN.

Electronic Materials and Processing
Room: 210E - Session EM-WeA

Interconnects: Methods and Materials for Removing Connectivity Constraints

Moderator: Andy Antonelli, Nanometrics, Michelle Paquette, University of Missouri-Kansas City

2:20pm **EM-WeA1 Interdiffusion Characterization of Selective Chemical Vapor Deposition Cobalt Cap and Copper**, ***Jeff Shu***, *Z. Sun, S. Choi, B. Yatzor, Z. Bayindir, G. Zhang, Y. Lee, H. Liu, J. Lansford*, GLOBALFOUNDRIES U.S. Inc.

Electromigration (EM) failure is always one of the key challenges of BEOL Cu interconnects. The continuous shrink of Cu feature size leads to higher current densities, which lower EM lifetimes. The interface between Copper and dielectric cap has been identified as the key diffusion path for copper atoms, and the adhesion of the interface is critical to EM performance. Different methods developed to improve the adhesion between copper and dielectric cap interface. One method of improving the adhesion has been the use of alloy seed, CuMn or CuAl. Mn (Al) will segregate and bond chemically to the copper and dielectric cap interface during dielectric cap deposition which can improve the adhesion of the interface and suppress Cu atoms migration along the interface under current stress. An alternate method of improving the adhesion is to have a self-aligned CoWP Cap or Selective CVD Co Cap on top of Cu which was developed for more stringent EM requirement of advanced nodes, such as 32nm, 20nm and beyond. Compare to self-aligned CoWP plating process, selective CVD Co Cap has higher selectivity and more compatible with porous ultra low k film. In this paper, we focus on interdiffusion characterization of selective CVD Co cap and copper. Co/Cu interdiffusion of cobalt films with different precursors are thoroughly evaluated and compared. Nitrogen content in Co film which enriches the grain boundaries due to low solubility in Co was identified as the key knob to control Co/Cu interdiffusion. Less nitrogen in Co film results in more copper diffusion. Better EM results on 20nm groundrule test structures demonstrated with higher nitrogen in Co film. Thermal anneal with H2 gas was found to be able to reduce nitrogen content in Co film which result in more Cu diffusion. Secondary Ion Mass Spectrometry (SIMS), X-ray photoelectron spectroscopy (XPS) and Electron Energy Loss Spectroscopy (EELS)/ Energy Dispersive X-ray Analysis (EDX) line scan were used for Cu diffusion characterization which clearly show Cu signal on top of Co film. A novel analytical technique of SIMS has been developed to characterize nitrogen content in Co film that CoN was selected as nitrogen detection molecular since nitrogen has some interaction with Co within the film.

2:40pm **EM-WeA2 Contact Engineering on Carbon Nanotube Interconnect Vias**, ***Yusuke Abe***, *A. Vyas, R. Senegor, C. Yang*, Santa Clara University

Nanocarbons such as carbon nanotubes (CNTs) and graphene are candidate materials for next-generation integrated circuit technologies due to their high current-carrying capacities and excellent electrical, thermal, and mechanical properties [1,2]. The key performance-limiting factor continues to be the high contact resistance at the interface with metal electrodes [3]. Metal depositions are frequently used during post-fabrication contact engineering for these nanocarbons to mitigate the high resistances between these materials and metal electrodes, with various degrees of success in achieving stable low-resistance contacts [4]. We have fabricated test devices for CNT vias, and measured their current-voltage (I-V) characteristics [5]. In this study, post-fabrication contact engineering is performed using electron-beam induced deposition of tungsten (EBID-W) [6] to improve the electrode contacts and hence reduce the total device resistance.

Fabrication of these via test structures without top contact metallization was described elsewhere [5]. In the present study, EBID-W is used to form the via top contacts (Fig. 1). From I-V and resistance measurements on 500 nm x 500 nm CNT vias with and without EBID-W top contact metallization, the effect of EBID-W contact on resistance reduction is clearly demonstrated (Fig. 2). While similar improvement can be obtained by current stressing without contact metallization [5], such technique would introduce an additional thermal cycle to the chip fabrication process and hence undesirable. On the other hand, the resistance of a via with W top contact is shown to have reached its minimum which is unaffected by further annealing (Fig. 3). Thus the contact resistance of the CNT via is indeed improved by top contact metallization with W, and that the resistance is stable. Without increasing the thermal budget from current stressing in chip fabrication, the use of EBID-W for via top contact metallization could facilitate the eventual functionalization of CNT via interconnects.

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3:00pm **EM-WeA3 Innovative Technological Solutions for Low-k Integration Beyond 10 nm**, ***Mikhail Baklanov***, IMEC **INVITED**

The general issue of porous low-k materials is degradation of their properties with the increasing porosity. The porous materials are soft, mechanically weak, and do not adhere well to silicon or metal wires. The large pore size also make them more sensitive to plasma damage (because of easy penetration of plasma species into the pores). All these challenges are becoming critical in advanced technology nodes when the distance between the metal wires has reduced to tens nm. This is the reason why the present efforts of researches and engineers are oriented to development and evaluation of new types of low-k materials. The materials need to have good mechanical properties, to have sufficient chemical and plasma resistance and small pore size. At the same time the research efforts are also oriented to development of new technological approaches reducing degradation of low-k materials during the integration. The invited talk will include 2 parts. 1. The first part of presentation includes the results of evaluation of new materials with low dielectric constant that are considered as potential candidates for future generations of nanoelectronic devices. These dielectric materials includes new generations of organosilicate glasses (Periodic Mesoporous Organosilicates (PMO), Zeolites and Metal-Organic Frameworks (MOFs). Fabrication of PMO materials is based on self-assembling chemistry and therefore it allows better control of critical properties of low-k materials. MOFs and Zeolites have very small pore size and unique mechanical properties. These materials have been developed in collaboration with several Universities. Their evaluation at imec includes measurement of their porosity and pore size (ellipsometric porosimetry – a technique patented by author), mechanical properties using Nanoidentation, chemical composition (FTIR, XPS, SIMS and some other techniques). Dielectric constant of these materials are measured my using metal-insulator-semiconductor (MIS) structures with Pt electrode. 2. The second part of the presentation is related to development of innovative technological approaches that are considered as key solutions for successful integration of porous low-k materials. Particularly, detailed analysis of recently patented cryogenic plasma etching of low-k materials will be reported. In this technology, the initial chemistries and reaction products are condensed in pores, makes the material dense and prevent penetration of plasma active into the bulk of low-k materials and reduce the plasma "damage". The results of evaluation have already been published in several papers. By using this technique the lowest integrated k-value of ultralow-k material has been achieved. Completely different integration scenario is considered for 5 nm technology nodes. The damascene technology can't work in this case because of plasma damage of low-k and the technology can return back to the subtractive approach with metal patterning. Although some industrial Companies are trying to develop technology of plasma etching of Cu, we are developing an alternative approach with metal patterning by using patterned sacrificial polymers. After metal deposition and planarization by chemical mechanical polishing , the sacrificial polymer is removed by using hydrogen plasma, then the trenches and vias are filled by ultralow-k dielectrics. The deposited low-k films is not exposed to plasma. The first results have been generated, the dielectric constants were achieved close to ones obtained cryogenic etch technology. However, some challenges still remain and they also will be highlighted.

4:20pm **EM-WeA7 Challenges and Directions for Dielectric Interconnect Materials for the 10nm node and Beyond**, ***Jeffery Bielefeld***, *J. Blackwell, S. Bojarski, M. Chandhok, J. Clarke, C. Jezewski, N. Kabir, S.W. King, M. Krysak, D.J. Michalak, M. Moinpour, A. Myers, J. Plombon, M. Reshotko, K. Singh, J. Torres, R. Turkot, H. Yoo*, Intel Corporation **INVITED**

To enable the continued scaling of interconnect layers for the 10nm node and beyond an increased number of materials and integration challenges will need to be addressed. Historically, interconnect dielectric materials have been broken down into Interlayer Dielectrics (ILDs) and Etch Stop (ES) / Hard Mask (HM) materials. The ILD layer is the major driver in capacitance improvement, while the ES layer enables patterning and acts as a diffusion barrier. In this paper, we will discuss two major challenges: (1) Pathways for the integration of porous low-k ILDs, and (2) Development needs for ES materials to enable improved patterning options.

The industry continues to work on the integration of low-k ILDs, but the momentum to implement these films has slowed in recent years due to the challenges of working with porous thin films. Low-k ILDs (k~2.0) exhibit 40-50% porosity with an interconnected pore network. The increased porosity can lead to damage and increased roughness during patterning, and can allow precursor penetration during the metal barrier deposition. To mitigate the problems of integrating a porous ILD, we have utilized the approach of pore stuffing. In this process, a sacrificial material is infiltrated into the pores of a fully cured ILD. The resultant film is non-porous with increased mechanical properties.

In this paper, we will discuss the challenges of finding a pore stuffing material that can fill the pores of the ILD, remain in place during dual damascene processing and can then be removed from the low-k ILD post metallization and CMP. In addition, we will show how pore stuffing improves trench profiles, and how it prevents metal penetration during barrier deposition. Finally the successful implementation of this process will be demonstrated and integrated capacitance improvement will be presented.

In a classic dual damascene flow, the ES layer is used as a diffusion barrier and as a patterning stop between ILD layers. To enable more advanced patterning and integration schemes, the role of these materials needs to be expanded. Specifically, there may be situations where multiple ES/HM materials are needed and with high etch selectivity to each other (>20:1). Etch selectivity values for typical materials (e.g. nitrides, carbides, amorphous silicon, metal hard masks and carbon hardmasks) are not currently sufficient. Development of new material options, deposition techniques and etch processes are needed. In this paper, we will discuss the current needs for new ES\HM materials and novel etch technology, along with our current progress toward this challenge.

5:00pm **EM-WeA9 Pore Sealing of Low-k Films by UV Assisted CVD Processes**, ***Priyanka Dash***, *D. Padhi*, Applied Materials

Porous ultra-low k (ULK) dielectric films with high porosity and larger pore size (k<2.4 and beyond) pose a serious challenge for their integration into next-generation microchips. In this paper, we report the formation of a thin layer of SiCxNy based pore sealing film deposited by UV assisted CVD. This film when deposited on damaged ULK surface assists in sealing the interconnected pores to prevent diffusion of metal liner and barrier metal precursors during the subsequent metallization steps. In addition pore sealing also enables an efficient sidewall protection to ULK thereby reducing its degradation by radical penetration during subsequent wet clean processes. A side benefit of this method is replenishment of depleted methyl species in damaged subsurface sites thereby improving hydrophobicity and recovery of k damage. A very thin pore seal film ~15 Ang is found to be sufficient to prevent metal precursor diffusion into a porous ULK k2.4 material. Porosimetry and backside SIMS were used to assess sealing behavior on surface pores of damaged ULK. On pattern wafers pore sealing treatment has been shown to significantly improve VBD and TDDB of k2.4 ULK to a level comparable to that observed for industry standard ULK k2.55 material. No structural change is observed in pattern CD for up to 15A of pore-seal deposition. Although this deposition is highly selective to surface sites available on damaged ULK, a thin layer (i.e. < 5A) of pore seal residue formed on Cu via bottom has been shown to be completely removed by typical CuOx wet clean solutions. Kelvin via measurements on structure wafers show that pore-seal with wet clean yields comparable via resistance as compared to wafers without pore-seal.

5:20pm **EM-WeA10 Copper Deposition and *In Situ* Chamber Cleaning using Pulsed-CVD Technique**, ***Fabien Piallat***, *J. Vitiello*, Altatech, France

Due to the conformity required for deposition of metals in high aspect ratio vias, Physical Vapor Deposition is replaced by techniques from the

Chemical Vapor Deposition (CVD) family. Conformity wise, the Atomic Layer Deposition (ALD) appears to be the best of the CVD techniques, but the low throughput is dissuasive for layers thicker than 10nm. At the edge between CVD and ALD, the Fast Atomic Sequential Technique (FAST) developed and patented by Altatech, enables deposition of layers with conformity close to the ALD at a higher throughput.

Through Silicon Vias are extensively used for interconnections and necessitate highly conductive materials in holes of aspect ratio higher than 10. Of all low-resistivity metals, namely Ag, Al, Au, Cu and W, studies showed that Cu is the best for filling trenches. Therefore, both the metal and the technique used are imposed, i.e. Cu deposition by CVD is the most suitable solution.

The main obstacle for a complete adoption of Cu as an interconnection metal is the difficulty to clean the chamber after process, since Cu cannot be etched by the usual fluorinated in-situ dry etching processes.

Successful deposition of conformal Cu layer was performed in vias with an aspect ratio of 10, using Altatech AltaCVD deposition chamber and a commercially available Cu precursor. Optimised deposition parameters resulted in low resistivity Cu, down to few μΩ.cm, with deposition rates higher than 100 $nm.min^{-1}$. Plotting the deposition rate depending on the substrate temperature highlighted an Arrhenius law behaviour, which in turn provided the optimal deposition temperature. Complementary SEM observation showed Cu layer with low roughness.

Futhermore, taking advantage of the Altatech pulsed solution, FAST, an in-situ dry cleaning process was developed using hexafluoroacetylacetone (hfacH) solvent. The main scheme for Cu etching comprise one step of Cu surface oxidisation and a second step where CuO_x compounds react with hfacH solvent to form volatile species. Several approaches were assessed; the following one will be presented and discussed:

O_2 and hfacH introduced simultaneously in the chamber

Alternation of O_2 plasma and hfacH fill

Pulsed alternation of O_2 and hfacH fill

O_2 plasma and pulses of hfacH

Optimising and understanding the influence of each process parameter was made possible by the use of a Residual Gaz Analyzer (RGA) and an Optical Emissions Spectrometer (OES). Cleaning efficiency at the particle generation level of all the approaches are compared, after few microns of Cu deposition and a chamber clean.

Finally, the efficiency of the most promising approach will be investigated on different chamber coatings.

5:40pm **EM-WeA11 Study of UV Impact on PECVD Non-Porogen ULK (Ultra low κ) SiCOH Film Nano-Structures, Film Mechanical and Electrical Properties**, ***Zhiguo Sun***, *J. Shu, S. Srivathanakul, H. Liu*, GLOBALFOUNDRIES U.S. Inc.

With the continuous shrinkage of back end of line (BEOL) metal pitches of sub-10nm technology node, integration with ultra-low κ (ULK) film becomes even more challenging. In comparison to traditional PECVD ULK films introduces pore through deposition with porogen precursor followed by UV or E-beam exposure to generate porosity , a new single precursor based ULK (ultra low κ) film has been formed without porogen and show promising on the sub 10nm technology road map . In this paper, we will use transmission Fourier Transform-Infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS) and Ellipsometric Porosimetry (EP) etc. to investigate the impact how different UV conditions will modify chemical bondings, film composition, pore structure and porosities. The role of UV in this new type of ULK film formation will be studied while difference UV conditions include UV bulbs and UV curing vacuum ambient etc. Film mechanical properties as well as electrical properties will be thoroughly compared. The interaction with downstream integration process steps, such as plasma induced damage and selectivity to MOCVD cobalt capping will be examined.

6:00pm **EM-WeA12 Bandgap Narrowing in Low-K Dielectrics**, ***Xiangyu Guo***, University of Wisconsin-Madison, *S.W. King,* Intel Corporation, *P. Xue,* University of Wisconsin-Madison, *J.-F. de Marneffe, M. Baklanov,* IMEC, Belgium, *V. Afanas'ev,* Catholic University of Leuven, Belgium, *Y. Nishi,* Stanford University, *J.L. Shohet*, University of Wisconsin-Madison

Electrical reliability in Cu interconnect structures has become a vital concern as the nano-electronics industry moves to sub-16 nm technology nodes and strives to implement insulating dielectric materials with increasingly lower dielectric constants (i.e., low-k). Studies have shown a direct correlation between trap/defect densities and electrical leakage of low-k materials,[1,2] , while the knowledge of the fundamental mechanism producing the damage is still limited. The bandgap energy, often serving as a reference point from which the presence and location of defect states in the bulk or at the interface can be understood, is of fundamental importance for understanding the electrical degradation in these dielectrics. In this work, core-level X-ray photoelectron spectroscopy (XPS) was utilized to determine the surface bandgap for various non-porous and porous low-k a-SiCOH dielectrics before and after ion sputtering by examining the onset of inelastic energy loss in core-level atomic spectra. Bandgap narrowing was observed in Ar+ ion sputtered low-k dielectrics. The reduction of bandgap energies ranges from 1.3 Ev to 2.2 Ev depending on the film composition. By examining the valence-band spectra measured with high-resolution XPS, we show that the bandgap narrowing in the low-k dielectrics is contributed to the arising and uplifting of the valence-band tail as evidenced by the presence of additional electronic states above the valence-band maximum (VBM). Electron spin resonance (ESR) measurements were also performed on the a-SiCOH films and the localization of each type of defect within the dielectric band gap is analyzed and compared. A combination of these results with the band gap measurements suggests the additional electron states contributing to the narrowed bandgap originate from carbon-related defects in the material. This work was supported by the National Science Foundation under Grant CBET-1066-231 and by the Semiconductor Research Corporation under Contract 2012-KJ-2359.

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Exhibitor Technology Spotlight
Room: Hall 1 - Session EW-WeA

Exhibitor Technology Spotlight Session
Moderator: Dennis Sollon, Kurt J. Lesker

4:00pm **EW-WeA6 Title Innovative Raman imaging**, ***Tim Prusnick***, RENISHAW, INC.

Renishaw's inVia is the world leader in confocal Raman spectroscopy. The inVia offers a wide range of imaging techniques that allow the user to choose the optimal solution for a particular sample type. Renishaw has partnered with other instrument vendors to combine atomic force microscopy (AFM) and scanning electron microscopy (SEM) to provide Raman analysis from the same point on the sample. The SEM Structural and Chemical Analyzer (SEM-SCA) combines both SEM and Raman techniques into one system, so that users can take full advantage of the high spatial resolution, large depth of field and high contrast afforded by the SEM, and the chemical information revealed by Raman. The Atomic Force Microscope (AFM) combine AFM and Raman to allow users to simultaneously acquire data from the same point on the sample without having to move it. This ensures that your data are consistent, even if your sample is changing with time.

Helium Ion Microscopy Focus Topic
Room: 210F - Session HI-WeA

GFIS Based Nanostructuring
Moderator: Shinichi Ogawa, AIST, Tom Wirtz, Luxembourg Institute of Science and Technology (LIST)

2:20pm **HI-WeA1 Nitrogen and Helium Gas Field Ion Source for Nanofabrication**, ***Marek Schmidt***, Japan Advanced Institute of Science and Technology, Japan, *K. Nagahara, O. Takechi, M. Akabori,* Japan Advanced Institute of Science and Technology, *A. Yasaka,* Hitachi High-Technologies Corporation, *T. Shimoda, H. Mizuta*, Japan Advanced Institute of Science and Technology

We report on the status and application of the gas field ion source (GFIS) focused ion beam (FIB) nanofabrication system [1] located at the Japan Advanced Institute of Science and Technology (JAIST). The atomic emission tip is biased against the extractor, generating high electric field strengths at the tip apex leading to ionization of the source gas. The ions are then accelerated to a typical energy of 25 Kv, focused, and scanned over the device under test (DUT). Such beams can be used to mill the DUT or generate images by simultaneous detection of the secondary electrons by the Everhart-Thornley detector. The GFIS-FIB employs a newly designed emission tip technology to use nitrogen ($N_2 \rightarrow N_2^+$) as a high sputter-yield source gas. Other ion species, such as helium and hydrogen, can be generated with the tip technology as well. The latter has been demonstrated to suppress the sub-surface damage formation [2], but is not currently in use at JAIST. Carbon is available for deposition, while iodine, xenon difluoride (XeF_2) and H_2O can be used for gas assisted milling.

Our current efforts involve carving graphene into sub-10-nm wide ribbons and electrically separating gold electrodes on top of graphene with the goal of realizing graphene tunnel field effect transistors. We also work on fabrication of graphene resonators based on suspended graphene that are narrowed down after the resist-based fabrication and hydrofluoric acid release. The second main area is the preparation of nanoimprint lithography (NIL) masters. Line-and-space pattern with a half pitch of 15 nm were milled into quartz substrates by the ion beam and will be applied to the fabrication of cutting-edge semiconductor devices. Lastly, we use the nitrogen ion beam for quantum point contact fabrication (QPC) in high-in-content InGaAs [3]. The size of the QPCs is ~30 nm × 150 nm, and the QPCs show step-like structures of $2e^2/h$ without magnetic field and of e^2/h and $3e^2/h$ with magnetic fields. Additionally, we will show the unique material contrast observed in nitrogen ion excited secondary electron images of graphene-based structures, and talk about low-energy operation, where 15 nm resolution has been achieved with a 5 Kv nitrogen beam. Such low energy beams will be used for defect generation and doping of graphene and other materials.

This work was partially supported by Kakenhi No. 25220904 from JSPS and the Center of Innovation Program from Japan Science and Technology Agency.

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[3] M. Akabori *et al.*, *Jpn. J. Appl. Phys.*, **53**, 118002, 2014.

2:40pm **HI-WeA2 Helium-Ion Milling of Gold Nanoantennas: Toward Plasmonics with Nanometer Precision**, ***André Beyer***, *H. Vieker,* Bielefeld University, Germany, *H. Kollmann,* Oldenburg University, Germany, *X. Piao, N. Park,* Seoul National University, Korea, *M. Silies, C. Lienau,* Oldenburg University, Germany, *A. Gölzhäuser*, Bielefeld University, Germany

Plasmonic nanoantennas are versatile tools for coherently controlling and directing light on the nanoscale. For these antennas, current fabrication techniques such as electron beam lithography (EBL) or focused ion beam (FIB) milling with Ga^+-ions routinely achieve feature sizes in the 10 nm range. However, they suffer increasingly from inherent limitations when a precision of single nanometers down to atomic length scales is required, where exciting quantum mechanical effects are expected to affect the nanoantenna optics. Here, we demonstrate that a combined approach of Ga^+-FIB and milling-based He^+-ion lithography (HIL) for the fabrication of nanoantennas offers to readily overcome some of these limitations (1). Gold bowtie antennas with 6 nm gap size were fabricated with single-nanometer accuracy and high reproducibility. Using third harmonic (TH) spectroscopy, we find a substantial enhancement of the nonlinear emission intensity of single HIL-antennas compared to those produced by state-of-the-art gallium-based milling. Moreover, HIL-antennas show a vastly improved polarization contrast. This superior nonlinear performance of HIL-derived plasmonic structures is an excellent testimonial to the application of He^+-ion beam milling for ultrahigh precision nanofabrication, which in turn can be viewed as a stepping stone to mastering quantum optical investigations in the near-field.

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3:00pm **HI-WeA3 Interactions of Focused Helium and Neon Ion-beams with Nanostructures**, ***Chung-Soo Kim***, *R.G. Hobbs, V.R. Manfrinato, A. Agarwal, K.K. Berggren,* MIT, *D. Wei*, Carl Zeiss NTS

Scaling the dimensions of materials to the nanoscale creates new opportunities and many applications. Nanomaterials display unique properties relative to their bulk counterparts due to surface/interface effects, quantum confinement/coherence, which have been investigated to understand new materials physics. Applications driven by nanostructures can benefit from their enhanced functionalities by modifying material properties and geometries via ion irradiation. Specifically in nanostructures, ion irradiation with a focused ion beam can play a critical role in modifying properties and geometries locally in those nanostructures. This local modification had already been proven to have applications in quantum optics and circuits by creating localized material modification at the nanoscale in bulk materials via focused helium ion beam (FHIB) irradiation However, local modification may occur in different ways in nanostructures. Therefore, one needs to investigate the effect of FHIB irradiation on nanostructures in order to control local modification in a desirable way and understand new physics.

In this work, we primarily study the interaction of a FHIB and nanostructures with two materials, single crystal silicon and diamond. Our experimental approach using thin vertical membranes fabricated by focused gallium ion beam enabled us to observe ion-nanostructure interaction in 3-dimension by preserving defects by ion irradiation. We have investigated new physical phenomena; (1) strain-induced volume expansion, (2) long-range ion propagation, and (3) material behavior's transition from a bulk to a small-scale where the size-dependent characteristic exists. We have explained these mechanisms between nanostructure (material, crystal orientation, and geometry) and helium ion (energy and dose). We have also extended our study to focused neon ion beam (FNIB) irradiation. We have investigated and compared the difference of ion-nanostructure interaction between neon and helium.

Furthermore, we have expanded our study to new nanofabrication method by embedding a 3D geometry on nanostructures with the consideration of a geometrical constraint, decided by crystal-to-amorphous boundary.

3:20pm **HI-WeA4 Polarization Control via He-ion Beam Induced Nanofabrication in Layered Ferroelectric Semiconductors**, ***Alex Belianinov***, *V. Iberi, A. Tselev, M,. Susner, M. McGuire, D.C. Joy, S. Jesse, A.J. Rondinone, S.V. Kalinin, O.S. Ovchinnikova*, Oak Ridge National Laboratory

Abstract

Rapid advanced in nanoscience rely on continuous improvements of manipulating matter at near atomic scales. Currently, well understood, robust resist-based lithography, carries the brunt of nanofabrication, however local electron, ion and physical probe methods are improving as well, driven largely in part of their ability to fabricate without multi-step preparation processes that can result in sample contamination from the resists and solvents. Furthermore probe based methods extend beyond nanofabrication to nanomanipulation and imaging, vital ingredients to rapid transition to testing and manufacturing of layered 2D heterostructured devices.

In this work we demonstrate that helium ion interaction in a Helium Ion Microscope (HIM) with the surface of bulk copper indium thiophosphate (CITP) $CuM_{III}P_2X_6$ (M = Cr, In; X= S, Se) result in the controlled loss of ferrielectric domains, and growth of cylindrical nanostructures with enhanced conductivity, with material volumes scaling to the dosage of the beam. The nanostructures are oxygen rich, sulfur poor, with the copper concentration virtually unchanged as confirmed by Energy Dispersive X-ray (EDX). Scanning Electron Microscopy (SEM) image contrast as well as Scanning Microwave Microscopy (SMM) measurements suggest enhanced conductivity of the formed particle, whereas Atomic Force Microscopy (AFM) based measurements indicate that the resulting structures have lower dissipation and a lower young's modulus.

Acknowledgements

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

4:20pm **HI-WeA7 Fabrication of Nanoscale Electronics with a Focused Helium Ion Beam**, ***Ethan Cho***, University of California, San Diego, *M. Ma,* Univeristy of California, San Diego, *C. Huynh,* Carl Zeiss Microscopy, LLC, *R.C. Dynes, S.A. Cybart*, Univeristy of California, San Diego

Since the invention of gas field ion source focused ion beams, researchers have had access to ion sources from inert gases. In particular, the focused helium ion beam (FHB) has a sub-nanometer beam spot that allows the direct patterning of nanometer scale devices without contamination. However, preparing samples with direct patterning is time consuming, especially when milling away large volumes of material. Here we demonstrate patterning a wide range of materials through disordering the crystal structure that only requires a dose orders of magnitude less than the milling dose. Patterning graphene has been difficult due to edge formation in the reactive ion etching step. Using a lower dose to perturb and disorder the carbon atoms would locally change the characteristics of graphene without destroying the integrity of the film. For materials that are hard to grow as a multilayer such as the iron based superconductor FeAs, the properties of conventional stacked Josephson junctions are limited by the film quality. With a FHB we can induce disorder in a very narrow region that suppresses the critical temperature (T_C) within this region to serve as the junction barrier. By removing the multilayer-processing the fabrication steps of these in-plane junctions are greatly simplified, and higher quality junctions are produced. Using disorder to create a lower Tc barrier also works for more metallic superconductors like MgB_2. For materials that undergo a superconductor-insulator transition, as for example cuprates, we demonstrate insulating in-plane tunnel junctions and nano wires. This technique also works for magnetic manganites that are sensitive to disorder. These materials have interesting characteristics at the interface between a multiferroic and magnetic material. Extensive care during the processing phase is required to preserve the interfacial properties. We demonstrate that the interface remains intact after a junction is fabricated with FHB. Most of the materials described above are extremely sensitive to processing, but by only locally altering the properties we eliminate interfacial problems and degradation due to heat generated in removing the material. Direct patterning using disorder induced from the FHB pushes the feature size truly to the nano meter scale, simplifies the fabrication both in time and number of steps, and preserves material integrity throughout the process. This FHB has the potential to be a general technology, and therefore allows us to engineer and study the fundamental physics of a variety of phenomena.

4:40pm **HI-WeA8 Creating and Imaging Nanosized Magnets using HIM and TEM Holography**, ***Gregor Hlawacek***, Helmholtz-Zentrum Dresden - Rossendorf, Germany, *F. Röder,* TU Dresden, *R. Bali, S. Wintz, R. Hübner, L. Bischoff,* Helmholtz Zentrum Dresden Rossendorf, *H. Lichte,* TU Dresden, *K. Potzger, J. Lindner, J. Fassbender*, Helmholtz Zentrum Dresden Rossendorf

Besides imaging, gas field ion source (GFIS) based microscopes [1] are used for materials modification. This usually is based on the use of high fluence to either mill the sample material or implant Nobel gas ions into the target

material [2].

Here, we present a novel route utilizing a Helium Ion Microscope (HIM) to form nano-sized magnets of arbitrary shape using very low fluences ($6x10^{14}$ cm^{-2}) of 20 keV-25 keV Neon ions. The fine Neon beam available in the HIM is used to locally switch 40 nm thin $Fe_{60}Al_{40}$ films from the well ordered paramagnetic B2 structure into the ferromagnetic A2 structure [3,4]. Planar structures potentially useful for applications such as spin valves or other spin--transport devices have been formed this way. Kerr Microscopy and off-axis TEM holography has been used to analyse the resulting magnetic nano-structures. Results on the energy depended depth of magnetization as well as on the lateral definition of the magnetic structures due to scattering are presented.

FR and HL gratefully acknowledge funding from the European Union Seventh Framework Programme under Grant Agreement 312483 - ESTEEM2 (Integrated Infrastructure Initiative - I3).

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5:00pm **HI-WeA9 Understanding Device Functionality in CVD-grown $MoSe_2$ Laterally Tuned with a Focused Helium Ion Beam**, ***Vighter Iberi***, *M.-W. Lin, X. Li, A. Ievlev, S. Jesse, S.V. Kalinin, A.J. Rondinone, D.C. Joy, K. Xiao, O.S. Ovchinnikova*, Oak Ridge National Laboratory

The scalability of electronic and information technology devices depends on the ability to tune layered materials. With the recent development of CVD-growth processes for high quality 2-dimensional materials, large scale fabrication has become routine. Monolayer molybdenum diselenide (MoSe2) has become a highly attractive candidate in the fabrication of functional electronic and optoelectronic devices due to its high electron mobility. However, critical is the structuring and functional tuning of these materials, as currently being done for semiconductors. Here, we will discuss the use of focused helium ion beams in tailoring the functionality of MoSe2 electronic devices with nanometer precision. Using a helium ion beam under high dosing allows for milling and structuring of MoSe2 devices with nanometer precision and prevents ion implantation and resist contamination effects. For lower helium ion doses we are able to tune the mobility as ascertained by local transport measurements. The nature of the associated properties of this material were explored using a combination of aberration-corrected scanning transmission electron microscopy (STEM), scanning probe microscopy (SPM) and optical spectroscopy techniques that provided insight into local mechanical, electromechanical, chemical and atomic structure properties of these devices and elucidate the effect of ion beam dose on device performance. Future perspective and scalability of this approach to device fabrication will also be discussed.

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.

Ref: K. Tan, S. Zuluaga, Q. Gong, Y. Gao, N. Nijem, J. Li, T. Thonhauser and Y. J. Chabal, *Chem. Mater.*, 2015, **27**, 2203-2217.

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).

MEMS and NEMS
Room: 211A - Session MN+AM-WeA

Emerging Materials & Fabrication Technologies toward Scalable & Additive Nanomanufacturing II

Moderator: Susan Burkett, The University of Alabama, Philip Feng, Case Western Reserve University

2:20pm **MN+AM-WeA1 Scalable Laser-Assisted Three Dimensional Printing of Nanomaterials**, ***Costas Grigoropoulos***, University of California at Berkeley **INVITED**

Nanomaterials and nanotechnology offer unique opportunities for fabricating devices of novel architecture and enhanced performance and can overcome system integration issues challenging current nanomanufacturing methods that are suited to planar geometries and are confined to top-down architectures. The central motivation of our work is to develop a new manufacturing method that offers scalability and flexibility enabling nanoscale device fabrication and integration in truly three-dimensional architectures over large areas and with arbitrary densities.

The core research strategy takes advantage of ultrafast laser beam processing for generating the scaffold multi-scale structures with 100 nm feature resolution. Two-photon polymerization is used to fabricate structures of tunable properties that are sensitive to pressure, light, heat and electrical stimulation. This technique, together with ultrafast laser micro/nanomachining will be adapted to multiple beam configurations in order to increase the processing throughput. Once the template is constructed, the directed self-assembly of block copolymers will be used to produce three-dimensional materials with tailored functionality where pattern amplification will be used to push the length scale to finer dimensions.

3:00pm **MN+AM-WeA3 Material Requirements and Challenges for NEM Logic Relays**, ***Tsu-Jae Liu***, University of California at Berkeley **INVITED**

The proliferation of mobile electronic devices and the emergence of applications such as wireless sensor networks and the Internet of Things have brought energy efficiency to the fore of challenges for future information-processing devices. The energy efficiency of a digital logic integrated circuit is fundamentally limited by non-zero transistor off-state leakage current. Mechanical switches have zero leakage current and potentially can overcome this fundamental limit. Contact adhesive force sets a lower limit for the switching energy of a mechanical switch, however, and also directly impacts its performance.

Stable operation with high endurance is a key requirement of switches for digital logic applications, and generally is a challenge for mechanical devices. The reliability of a miniature relay is limited not by structural fatigue or dielectric charging, but by contact oxidation or stiction.

This invited talk will begin with a review of recent progress toward the development of a reliable nano-electro-mechanical (NEM) relay technology for digital logic applications. It will then discuss the influence of contacting electrode material properties on relay performance and reliability. Opportunities for ultra-low-power computing with relays will be described.

4:20pm **MN+AM-WeA7 Microplasma-based Direct-write Patterning Processes for Additive Microfabrication**, ***Christian Zorman***, Case Western Reserve University **INVITED**

Metals comprise the most versatile and widely used class of materials in micro- and nanosystems, serving as electrical contacts, interconnects, electrodes, and even mechanical components. The most commonly used method to fabricate metallic structures involves physical vapor deposition combined with photolithography. This subtractive approach is effective in producing device structures with high pattern fidelity; however, such processes are limited by modest throughput, use of aggressive chemicals and high material wastage. Reliance on vacuum-based deposition processes limits process scalability and can hinder adoption in cost-sensitive applications. The emergence of flexible electronics has stimulated the development of additive approaches such as ink-jet printing for depositing patterned metal structures. Printing is attractive for such applications because it is performed under ambient conditions and can be integrated into large-scale roll-to-roll systems. However, the inks can be expensive and the variety of materials that are available as inks is limited. In addition, the organic capping agents that are used to stabilize nanoparticle-based inks are difficult to remove, which can compromise conductivity and mechanical integrity. Removal of the organics requires post-deposition processes that can limit the usage of certain polymer substrates. Adhesion of the printed structures to the substrates can also be a significant issue, especially in flexible applications.

This paper describes two novel microplasma-based processes under development at Case Western Reserve University to fabricate patterned metallic structures with micro- to nanoscale dimensions on rigid and flexible substrates. Our principal process utilizes electrons extracted from an atmospheric pressure microplasma to electrochemically reduce metal ions within a polymer substrate, selectively forming continuous metallic structures within that polymer. Recently, we have developed a microsputtering process that uses ions generated by an atmospheric-pressure microplasma. This process capitalizes on a physical vapor that is generated within a small capillary by Ar ion bombardment of small diameter metal wires. Forced Ar flow aids in the ejection of the resulting physical vapor through the orifice, which is positioned in close proximity to the substrate. Both processes are performed under ambient conditions thereby offering the same advantages as ink-jet printing, including potential scale-up to roll-to-roll processing. This presentation will detail the two processes and summarize most recent results in creating and characterizing micropatterned metal structures on a variety of substrates.

5:00pm **MN+AM-WeA9 Ni-induced Graphitization for Enhanced Long-term Stability of Ohmic Contact to Polycrystalline 3C-SiC**, *S. Chen, L.E. Luna,* University of California at Berkeley, *Z. You,* Tsinghua University, *C. Carraro,* ***Roya Maboudian***, University of California at Berkeley

Micro- and nano-electromechanical systems (M/NEMS) technology enables a diverse range of physical and chemical sensing under conditions close to ambient. However, there is a growing interest in sensors that can operate under harsh environments, including high temperature, high pressure, extreme radiation and corrosive. Sensing within these environments necessitates a robust semiconductor platform, different from those employed in traditional Si-based M/NEMS. A robust material, such as silicon carbide (SiC) provides compelling advantages not achievable with Si-based devices. SiC is a wide bandgap semiconductor with excellent mechanical, chemical and electrical stability, and thus is well suited for designing devices capable of operation in many harsh environments. Yet, harsh-environment stable metallization remains one of the key challenges with SiC technology. Here, we present a novel metallization scheme, utilizing solid-state graphitization of SiC, to improve the long-term reliability of Pt/Ti contacts to polycrystalline n-type SiC at high temperature. The metallization scheme includes an alumina protection layer and exhibits low stable contact resistivity even after long-term (500 hr) testing in air at 450 °c. This study provides a feasible fabrication method and discusses the role of induced graphitic layer on contact stability.

5:20pm **MN+AM-WeA10 Fabrication of High Aspect Ratio Millimeter-Tall Free Standing Post Arrays using Carbon-Nanotube-Templated Microfabrication with a Sacrificial Hedge**, ***Guohai Chen***, *R. Vanfleet, R.C. Davis*, Brigham Young University

Carbon-nanotube-templated microfabrication (CNT-M) has shown precise high aspect ratio features in interconnected geometries.[1] However, the feature of isolated posts remains challenging.[2] Here we developed a process which involves fabrication of CNT posts connected by supporting hedges using CNT-M followed by oxygen plasma etching to remove the sacrificial hedges. We have explored the fabrication of posts with diameters from 10-40 um and heights up to 1.3 mm using sacrificial hedges of 1-5 um in width. With the CNT template, isolated free standing posts from a variety of materials can be made. For example, silicon or silicon nitride posts can be fabricated by infiltrated with silicon or silicon nitride. The creation of hybrid carbon/metal (copper, nickel) posts can also be realized through pulse electroplating.

1. J. Song, et al. Carbon-Nanotube-Templated Microfabrication of Porous Silicon-Carbon Materials with Application to Chemical Separations. Adv. Funct. Mater., 2011, 21, 1132.

2. K. Moulton, et al. Effect of iron catalyst thickness on vertically aligned carbon nanotube forest straightness for CNT-MEMS. J. Micromech. Microeng., 2012, 22, 055004.

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.

This work is supported in part by DOE Grant DE-FG02-07ER15842.

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.

This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences through grant

number: DE-FG02-96ER45576

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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[4] M. O. Ozbek, J. W. Niemantsverdriet, *J. Catal.,***2014,** *317,* 158

[5] G. J. A. Mannie, L. Lammich, Y. W. Li, J. W. Niemantsverdriet, J. V. Lauritsen, *ACS Catal.,***2014,***4,* 3255

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 nanosheres 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.

References:

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Plasma Science and Technology
Room: 210B - Session PS+AS+SS-WeA

Plasma Surface Interactions
Moderator: Steven Vitale, MIT Lincoln Laboratory

2:20pm **PS+AS+SS-WeA1 *In Situ* FTIR Diagnostics and Characterization of Etch By-Product Deposition on Chamber Walls and Wafer Surface during Halogen Etching of Silicon**, ***Neema Rastgar***, *S. Sriraman*, *R. Marsh*, *A. Paterson*, Lam Research Corporation

Plasma etching is a critical technology for nanoelectronics fabrication, but the use of a vacuum chamber limits the number of in situ, real-time diagnostics measurements that can be performed during an etch process. Byproduct deposition on chamber walls during etching can affect the run-to-run performance of an etch process if there is build-up or change of wall characteristics with time. Knowledge of chamber wall evolution and the composition of wall-deposited films are critical to understanding the performance of plasma etch processes, and an in situ diagnostics measurement is useful for monitoring the chamber walls in real time.

In this talk, we report the use of attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) to perform in situ diagnostics of a vacuum chamber's walls during plasma etching. Using ATR-FTIR, the relative thickness and makeup of chamber wall deposits in real time is monitored. This information is then used to develop a chamber wall cleaning process in order to maintain reproducible etching conditions from wafer to wafer. In particular, we report mid-IR (4000-650 cm^{-1}) absorption spectra of chamber wall-deposited silicon byproducts formed during halogen etching of silicon wafers. Preliminary results demonstrating measurements of on-wafer etch byproduct evolution as well as its correlation to chamber wall deposits will be discussed.

2:40pm **PS+AS+SS-WeA2 Particle as a Temperature Probe: Thermal Effects in Non-Thermal Plasmas**, ***Thomas Lopez***, *L. Mangolini*, University of California Riverside

Silicon nanocrystals are currently under investigation for several applications including nanoelectronics, light emitting devices, photovoltaics, thermal electric devices, and energy recovery and storage. Continuous flow nonthermal plasmas reactors are ideal for silicon nanaparticle production for many reasons; continuous flow non thermal plasma reactors are a scalable system, they readily produce completely amorphous to completely crystalline samples, and they have the ability to control size and size distributions of produced particles [1]. Extensive *in-situ* and *ex-situ* characterization on continuous flow non-thermal plasma reactors has been carried out characterizing nucleation, growth, and structural evolution [2]. Particle size, structure, and surface termination are all particle properties that are directly correlated to the particles' interactions with ions and other plasma produced radicals during their creation [2]. It has been shown that the interactions between particles, ions and other radicals in non-thermal plasmas leads to a thermal annealing process [3], meaning particles in non-thermal plasmas are heated well above the temperatures of their respective carrier gases. We probe the temperature of silicon nanoparticles produced via continuous flow non-thermal plasma reactors by monitoring their surface termination. *In-situ* FTIR has been utilized to track changes in the surface chemistry of particles, which have then been correlated to the particle temperature as a function of plasma power. FTIR data shows that hydrogen termination of silicon nanoparticles as they flow through a plasma is power dependent, with higher power leading to a decrease in hydrogen surface termination. We attribute this behaviour to thermally induced desorption from the particle surface. A discussion on the characterization of nanoparticle interactions with the plasma based on *in-situ* FTIR, optical emission spectroscopy and ion density measurements will be presented.

1. Lopez, T. and L. Mangolini, *Low activation energy for the crystallization of amorphous silicon nanoparticles*, Nanoscale, 2014. **6**(3): p. 1286-1294

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3. Kramer, N.J., R.J. Anthony, M. Mamunuru, E.S. Aydil, and U.R. Kortshagen, *Plasma-induced crystallization of silicon nanoparticles*, Journal of Physics D: Applied Physics, 2014. **47**(7): p. 075202.

3:00pm **PS+AS+SS-WeA3 Plasma-Surface Interactions at Low and High Pressure**, ***Vincent Donnelly***, University of Houston **INVITED**

This talk will review studied of the interactions of low pressure Cl_2, HBr, and O_2 inductively-coupled plasmas with reactor chamber walls, with and without Si etching, using the "spinning wall" technique. The spinning wall is part of the reactor chamber walls, allowing near-real-time analysis of the composition of surface layers via Auger electron spectrometry, and determination of species desorbing off the walls by mass spectrometry. Langmuir-Hinshelwood (L-H) reactions, with surface residence times > 0.5 ms can be studied by this technique. Many commonalities were found for the different source gas plasmas. For example, when the walls were coated with SiO_x or AlO_x layers, A + B recombination reactions including O + O, O + Cl, Cl + Cl and H + Br are detected, provided that the surface contains a level of oxygen above some critical value. During Si etching, surfaces coated with Si-halide products tend to be less catalytic toward L-H recombination reactions, while Si-oxyhalides films formed on chamber walls when oxygen is present in the plasma are much more active in promoting L-H recombination, as well as adsorption and delayed desorption of Cl_2. At most sites, O is believed to be in the inactive form of Si-O-Si. In relatively few cases, O cannot coordinate to a second Si and the active Si-O- forms. This quickly forms Si-O-A and then mobile B on the surface forms Si-O-AB, followed by desorption of AB, which could also be delayed. For all of the products observed, formation and desorption of AB is exothermic. Si etching with small oxygen addition leads to "sticky" products with a range of masses up to at least the limit of our mass spectrometer (m/e = 500) that desorb from chamber wall surfaces in ms to min after plasma exposure. Gaseous products contain -O-Si-O- linkages are prominent, in addition to Si-mono and tri-halides. In HBr-containing plasmas, products contain little or no H. Experiments have also begun to study plasma-surface interactions at atmospheric pressure. Species present within one mean free path of a quartz substrate exposed to a He jet plasma in ambient air and in a sealed chamber with gas additives are spatially resolved using a new near-field optical emission spectroscopy method.

4:20pm **PS+AS+SS-WeA7 Measurements of IIEE Emitted Electrons from Chemically-Cleaned and Sputtered-Cleaned Semiconductor Surfaces**, *D. Urrabazo, **Lawrence Overzet***, University of Texas at Dallas

Plasma-surface interactions with semiconductors comprise a variety of interesting phenomena in addition to etching and deposition. One such phenomenon is ion induced electron emission (IIEE). IIEE has historically been viewed as extremely surface sensitive; but recent measurements have suggested that the IIEE yield from semiconductors, unlike metals, may in fact depend on the sub-surface properties as well. We investigated the effects of the surface and sub-surface properties (doping type, Fermi level, cleanliness level) on the relative IIEE yields from Si and Ge. Our measurements indicate that the relative IIEE yields did not depend on the doping type to a significant degree independent of the level of cleanliness. This result is consistent with IIEE theory. We further explored the sensitivity of the IIEE yield to surface cleanliness by making XPS and UPS measurements on the surface chemistry and approximate surface density of states (sDOS) of the semiconductors. By combining the theoretical IIEE model with the sDOS, we were able to replicate the changes in the IIEE emitted electron distribution functions due to surface cleanliness changes. Thus, we confirmed that the IIEE yield is affected by the cleanliness of the surface primarily through the change in the surface density of states.

Acknowledgement: This material is based upon work supported by the Department of Energy under Award Number DE-SC-0009308.

4:40pm **PS+AS+SS-WeA8 Effects of Hydrogen on Etching Processes for Transparent Conducting Films**, ***Hu Li*****, *K. Karahashi,* Osaka University, Japan*, M. Fukasawa, K. Nagahata, T. Tatsumi,* Sony Corporation, Japan*, S. Hamaguchi*, Osaka University, Japan

The market demand for high-resolution optoelectronic devices such as head-mounted displays has accelerated the development of micro pattern formation technologies for transparent conducting oxides (TCOs) with a pattern resolution of sub-microns or even nanometers. Reactive ion etching (RIE), which has been widely used in the fabrication of semiconductors, is also a promising technology for patterning of TCOs. Tin-doped indium oxide (ITO) and Zinc oxide (ZnO) are widely used TCOs in the industry. The goal of this study is therefore to establish RIE technologies for ITO and ZnO for high-resolution patterning.

Typical RIE processes for ITO and ZnO use plasmas based on organic gases such as CH_4 and CH_3OH. CH_4 and CH_3OH are non-corrosive gases and RIE processes with such gases are expected to achieve high etching rates with less process damages. In this study, we have mostly focused on ZnO etching processes and evaluated sputtering yields and analyzed surface reaction characteristics of ZnO by various chemically reactive species such as CH_x^+, H^+, and H^*, using a mass-selected ion beam system. The mass-selected ion beam system allows one to examine surface reactions caused by specific ion species with a given incident energy incident upon the sample substrate set in an ultra-high vacuum (UHV) reaction chamber. Simultaneous injection of hydrogen radicals have been also performed with a hydrogen radical source. Surface chemical composition after such beam injections have been analyzed by *in-situ* X-ray Photoelectron Spectroscopy (XPS) installed in the reaction chamber.

Our previous study [1] found that the sputtering yield of ZnO strongly depends on the number of hydrogen atoms contained in each incident molecular ions. In this study, we have clarified the effects of incident hydrogen ions and radicals. When ZnO is etched by simultaneous injection of energetic CH^+ ions and abundant hydrogen radicals, it has been found that etching proceeds with no carbon deposition and the sputtering yield of ZnO is closed to that of the corresponding physical sputtering. This result suggests that hydrogen radicals prevent carbon accumulation on ZnO and energetic hydrogen ion incidence leads to the formation of a surface damage layer, which is more easily sputtered by incident energetic ions. Therefore the presence of CH_3^+ ions is not indispensable in such a RIE process and the embrittlement of ZnO by hydrogen is more crucial to the achievement of efficient etching processes for ZnO.

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5:00pm **PS+AS+SS-WeA9 Mechanisms of Hydrocarbon Based Polymer Etch using Pulsed Plasmas**, ***Barton Lane****, P. Ventzek, M. Matsukuma, A. Suzuki, A. Koshiishi*, Tokyo Electron Limited

Dry etch of hydrocarbon based polymers is important for semiconductor device manufacturing. The etch mechanisms for oxygen rich plasma etch of hydrocarbon based polymers has been studied but the mechanism for lean chemistries has received little attention. We report on an experimental and analytic study of the mechanism for etching of a hydrocarbon based polymer using an Ar/O2 chemistry in a single frequency 13.56 MHz test bed. The experimental study employs an analysis of transients from sequential oxidation and Ar sputtering steps using OES and surface analytics to constrain conceptual models for the etch mechanism. The conceptual model is consistent with observations from MD studies and surface analysis performed by Vegh, et al. and Oehrlein, et al. [1,2] and other similar studies. Parameters of the model are fit using published data and the experimentally observed time scales. [1] J.J. Vegh, D. Nest, D. B. Graves, R. Bruce, S. Englemann, T. Kwon, R. J. Phaneuf, G. S. Oehrlein, B. K. Long, and C. G. Willson, Jour. of Applied Physics **104**, 034308 (2008), [2] G.S. Oehrlein, R. J. Phaneuf, D. G. Graves, J. Vac. Sci. Tech. B 29, 010801-1 (2011).

5:20pm **PS+AS+SS-WeA10 Role of Plasma Density in Damage Characterization and its Impact on Low-Damage Plasma Process Design**, ***Koji Eriguchi****, M. Kamei, Y. Nakakubo, K. Ono*, Kyoto University, Japan

Plasma process-induced damage (PID) is one of critical issues in designing metal−oxide−semiconductor field-effect transistors (MOSFETs) with higher performance and reliability. The damage creation mechanisms—plasma-induced physical damage (PPD) and charging damage (PCD) [1]—have been characterized by various techniques so far [2] to design low plasma processes. In this study, conflicting results leading to erroneous conclusions in designing future plasma processes are presented, where ion flux and charge injection from plasma (~ plasma density) play a key role in these conventional characterizations. Firstly, regarding PPD, n-type (100) Si wafers were exposed to Ar-based ICP and CCP discharges [3] and the localized defects were created in the Si substrates by ion bombardment. It is found that, although the average energy of incident ions (E_{ion}) is larger for the case of CCP, the latent defect density (n_{dam}) of CCP-damaged samples is smaller than that of ICP, even after the damaged-layer removal. This observation is in sharp contrast to previous pictures, i.e., the larger E_{ion} leads to the larger PPD. Secondary, MOSFETs with "high-k" ($HfSiO_x$) gate dielectric were damaged by the Ar-based ICP plasma and the high-k damage (~ carrier trap site generation) by PCD is evaluated by time-dependent dielectric breakdown (TDDB) measurement [4]. We identify that the TDDB lifetime becomes longer under a certain amount of charge injection by plasma-induced current. This finding implies that one might be misled to an erroneous design rule of future LSIs. We propose a model explaining these conflicting results, where both ion flux and charge injection from plasma and the nature of the analysis techniques are taken into account. Since modern FinFETs with high-k dielectrics [5] are susceptible to PPD and PCD, the present model should be intensively implemented in designing future "low-damage" plasma processes.

This work was supported in part by a Grant-in-Aid for Scientific Research (B) 25630293 from the Japan Society for the Promotion of Science.

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5:40pm **PS+AS+SS-WeA11 Dry Deep Etching Of Bulk Titanium By Plasma Processes**, ***Edouard Laudrel****, T. Tillocher, P. Lefaucheux,* GREMI CNRS/Université d'Orléans, France*, B. Boutaud,* Sorin Crm, France*, R. Dussart*, GREMI CNRS/Université d'Orléans, France

Bio-MEMS have emerged these last years with applications for biosensors, drug delivery, etc. The biocompatibility, the mechanical strength and the hydrophilicity properties have made titanium a widely used material with a great interest in the biomedical field. This element was chosen to fabricate body implantable devices with the help of microfabrication methods from microelectronics technologies in order to pattern structures with vertical sidewalls and smooth surfaces. Most of the literature with an interest in titanium deep etching relies on chlorine plasma processes. They are performed at room temperature of the substrate with typical etch rates close to 1 µm.min^{-1} and provide rather smooth surfaces. TiO_2 or Ni are typically used as hard mask. However, a thick (several 10s of microns) SU8 layer, which is a negative photoresist, has also been reported as an alternative mask because it can be easily patterned and stripped.

*** Coburn & Winters Student Award Finalist**

Samples used in our experiments consist of coupons of a patterned titanium wafer glued on a silicon carrier wafer. The titanium wafer is 300 µm thick with a 15 µm thick backside thermal TiO_2 layer and the mask is a 15 µm electrochemically deposited thick nickel layer. The samples were processed in two different ICP reactors. Two different chemistries can be used to etch titanium. A chlorine-based chemistry at low pressure can be used to obtain anisotropic profiles but with reduced etch rates at room temperature. With the first reactor, equipped with a diffusion chamber, titanium etch rate was 1 $\mu m.min^{-1}$. A fluorine-based chemistry admits higher etch rate (as 4 $\mu m.min^{-1}$) at higher pressure (few Pa) with isotropic profiles if the sample temperature is sufficient to form volatile etch by-products. Both chemistries, as well as $Cl_2/Ar/SF_6$ mixture, produced non-reproducible results and a high roughness. These observations were attributed to the redeposition of etch by-products (like $SiOCl_x$) on the sample surface. It induces a micro-masking effect which generates a high roughness and leads to reproducibility issues. The so-called APETi (Alternated Process for the deep Etching of Titanium) process has been developed to prevent this roughness and increase the reproducibility. An average etch rate of 1.4 $\mu m.min^{-1}$ has been achieved with reproducible features.

Comparative experiments have started on a second ICP reactor which enables higher etch rates due to a higher self-bias voltage and higher density species. The substrate holder temperature can also be higher, which should help to enhance chemical etching processes with a fluorine chemistry.

6:00pm **PS+AS+SS-WeA12 Particle Transport with Wafer Potential Controlled by Dipole Electrostatic Chuck Electrodes**, ***Masaki Ishiguro***, *M. Sumiya*, Hitachi High-Technologies Corp., Japan

In plasma etching for semiconductor manufacturing, it is important to prevent particle attachment on the wafer during processing to maintain high yield rate. As the device size continue to be scaled down, smaller particles should be taken care not to attach onto the wafer. It is said that 10 nm particles will be critical for semiconductor manufacturing in 2019 [1]. One important approach to prevent particle attachment on the wafer is controlling particle transport. Electrostatic force is one of the suitable forces to control particle transport. In the case that particle charge and wafer potential polarity is opposite, large number of small particles can be attracted onto the wafer. In plasma etching process, plasma on and off periods are periodically repeated. Kobayashi *et. al.* revealed that in plasma on period, the particles are trapped at the plasma sheath boundary and there is a less-risk of particle attachment to the wafer [2]. It suggested that, in plasma off period, there is a large-risk of particle attachment to the wafer if the wafer and the particles have opposite charge respectively.

In this study, the relationship between particle attachment to the wafer and wafer potential in plasma off period was investigated. Particle count on the wafer was measured at different wafer potential during plasma-off period by changing voltage settings of dipole electrostatic chuck electrodes (ESC) in Ar, O_2 and N_2 plasma. In the case of negative wafer potential, particle counts increased as the plasma off time was prolonged. On the other hand, in the case of positive or 0 wafer potential, particle count was relatively low level and it did not increase even if plasma off time was prolonged. This result suggests that, in our experimental condition, the particles charge positive during plasma off period and they are continuously generated from inner chamber wall. If the wafer has negative potential, the particles are attracted by electrostatic force. The numerical simulation result will also be shown to understand the effect of electrostatic force on small particle attachment.

In plasma on period, wafer has plasma floating potential and the potential remains on the wafer even after plasma discharge is finished. It leads to increase of particle attachment risk as mentioned above. In this time, newly developed wafer potential control sequence with ESC electrodes to reduce wafer potential during plasma off period will be reported. This sequence enables to reduce particle attachment during plasma off period.

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Plasma Science and Technology
Room: 210A - Session PS+TF-WeA

Plasma Deposition and Plasma Assisted ALD
Moderator: Sumit Agarwal, Colorado School of Mines

2:20pm **PS+TF-WeA1 Plasma Prize Talk: Plasma Processing of Materials: What makes Plasma Special and Future Outlook?**, ***Richard van de Sanden****, DIFFER **INVITED**

Plasma processing of materials is at the heart of present day technologies such as found in the manufacturing of IC's, liquid crystal displays and large scale production of solar cells, to name only a few. For a basic understanding of the key processes determining the processing quality advanced in situ diagnostics for both the plasma phase as well as diagnostics to characterize the plasma-surface/material interaction are required. This basic understanding will enable control over these processes, such as the controle of the ion energy distribution function by tailoring the bias voltage on the materials processed.

The aspects which differentiates plasma processing from other processing technologies such as the presence of charge, short living reactive radicals and nonequilibrium species distribution to name a few, will be discussed. In a future outlook I will argue that the nonequilibrium aspects, especially connected to the vibrational populations in molecular plasmas, are not yet exploited to its full extent. If we succeed in controlling the population of the vibrational states many novel applications in catalysis, gas and surface processing of materials come within reach.

3:00pm **PS+TF-WeA3 Feature Scale Simulation of Atomic Layer Deposition via FPS3D**, ***Paul Moroz,*** Tokyo Electron US Holdings, *D.J. Moroz*, University of Pennsylvania

Atomic layer deposition (ALD) allows accurate atomic-scale deposition of materials layer-by-layer with almost conformal feature profiles. Together with atomic-layer etching (ALE), it provides the tools necessary for satisfying the ever increasing demands for improved accuracy and miniaturization, and is becoming one of the leading methods among advanced semiconductor technologies. ALD requires cycling processing, with each cycle consisting of at least two timesteps, each timestep having its own parameters corresponding to different fluxes of species and different surface chemistry. Numerical simulation of ALD could be accomplished at the levels of quantum chemistry (QC), molecular dynamics (MD), or feature-scale (FS) calculations. While QC provides an ab-initio approach, MD depends on approximations of interactions with inter-atomic potentials, and FS methods rely on reactions between species. The reactions used in FS simulations could be estimated from experiments or they could be taken from MD or QC calculations. We present here numerical simulations of ALD for the case of deposition of silicon nitride film onto silicon utilizing dichlorosilane gas and ammonia plasma. Our calculations were carried out via the feature-scale simulator FPS3D [1-3], which can efficiently simulate multi-timestep operations and which allowed us to replicate the results of considered ALD experiments. In correspondence with the experiments, the reactions were selected such that the deposition of a single monolayer was produced not in a single cycle, but in two cycles, even when the duration of each timestep was long enough for the processes to saturate. FS simulations run much faster and can operate on a much larger scale than can MD and, especially, QC methods. FS methods can efficiently simulate processing of entire features with complex profiles both in 2D and 3D. We simulate the feature profiles obtained during processing at different conditions and initial settings, and we discuss various effects which could change the roughness of profiles. We also analyze the effects of partial conformity of obtained profiles and the effects of incomplete ALD, during which some reactions may not self-limit due to insufficient processing time.

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3:20pm **PS+TF-WeA4 Plasma Enhanced Atomic Layer Deposition Applications using an Ion Source**, *F. Papa,* Gencoa USA*, V. Bellido-Gonzalez, H. Li,* Gencoa Ltd, UK*, HD. Ngo,* University of Applied Sciences Berlin, Germany*, K. Kröhnert,* Fraunhofer Institut IZM Berlin, Germany*, O. Ehrmann, K.D. Lang, P. Mackowiak, Piotr,* TU Berlin, Germany, ***William Sproul***, Reactive Sputtering, Inc

Atomic Layer Deposition (ALD) has been slowly gaining acceptance in the field of thin film deposition. Although firstly described in the 1960's as molecular layering by researchers in the former USSR, the introduction of

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*** PSTD Plasma Prize**

the technology to the world came via Tuomo Suntola's group in 1974 (**1**). The application to ZnS highly ordered films was a real success, and made the electroluminescent displays a reality. Since then the concept has been applied into other technology areas. There are many benefits of ALD, however, in terms of deposition rates, film stress and management of reactive gas species in complex 3D structures there is still a long road ahead.

In order to lower the film stress plasma technology has been applied. Plasma Enhanced ALD (PEALD) has been introduced in order to lower the temperature requirements for the ALD process and also in order to control the properties of the ALD deposited film. The industrialization of such process presents a number of challenges. In PEALD, it is of interest to control the nature and degree of interaction of such plasmas with the surface chemistry. Plasma sources which can control the energy of the ion beam are of special interest. Also, from the industrialisation point of view the sources would need to be able to upscale the process. For those reasons, the authors believe that a Linear Ion Sources (LIS) could help move ALD processes into mass production. LIS's have been slowly pushing their way through into vacuum coating technology market for over 15 years. Only last year a small circular ion source, which can replicate the functional properties of large LIS's was introduced (**2**). This development has enabled rapid transitions from prototyping to manufacturing. The use of such a source is interesting for PEALD as the processes developed in the lab could be easily implemented at an industrial level. As part of the investigation the authors have used the ion source PEALD process on etched silicon wafers in order to produce low temperature conformal depositions. The wafers were etched with different features, like deep aspect ratio trenches, which are of great interest in today's semiconductor devices. Results will be presented.

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4:20pm **PS+TF-WeA7 Plasma-Assisted ALD of SiN$_x$: The Surface Chemistry Studied by Infrared Spectroscopy**, ***Roger Bosch***, *L.E. Cornelissen, C.K. Ande, W.M.M. Kessels*, Eindhoven University of Technology, The Netherlands

Silicon nitride (SiN$_x$) deposited by ALD is gaining a lot of interest lately, as it allows for conformal films prepared at low temperatures while maintaining a high film quality and uniform thickness. This is challenging for conventional deposition techniques, such as CVD and PECVD. Within the work presented in this contribution, the growth of SiN$_x$ by ALD and the associated surface chemistry have been studied. The chosen plasma-assisted ALD process employs bis(tertiary-butylamino)silane ($SiH_2[NHC(CH_3)_3]_2$,BTBAS) as precursor and N_2 plasma as co-reactant. Various *in situ* studies have been performed and the experimental work has been complemented with DFT calculations.

More particularly, to study the surface chemistry we developed a versatile setup, which combines ALD with Fourier transform infrared spectroscopy. A sample manipulator was designed that enabled us to study the species present at the surface, with a submonolayer sensitivity, as a function of substrate temperature (100-300°C) and incident angle of the IR beam. The setup also allowed for gas phase measurements.

Gas phase infrared measurements have been performed to identify which species were present in the reactor after the precursor dose and N_2 plasma exposure. The measurements revealed that *tert*-butylamine ($(CH_3)_3CNH_2$) is the main reaction product after precursor exposure. This indicates that the Si-N bond in the precursor molecule breaks when it interacts with active sites at the surface.

Surface infrared measurements have been conducted at different temperatures to determine which species were present at the surface after one of the ALD half cycles, i.e. after the BTBAS half cycle and after the N_2 plasma half cycle. Amongst others, a pronounced density of Si-H at the surface has been established, and at lower temperatures (~100°C) also a signal from C-H groups was clearly observed after BTBAS dosing. From these infrared measurements, complemented with DFT calculations and additional thin film studies, we propose a mechanism for the growth of SiN$_x$ by ALD using BTBAS and N_2 plasma, which will be discussed during the presentation.

4:40pm **PS+TF-WeA8 Structural Characterization of Surface Dielectric Barrier Discharges (SDBD) for Atmospheric Pressure Plasma Enhanced Spatial ALD (PE-S-ALD)**, ***Yves Creyghton***, *J. Emmelkamp, F. Roozeboom*, TNO Technical Sciences, Netherlands

Spatial ALD (S-ALD) is an emerging technology with substrates passing a series of spatially separated gas injector zones. This concept enables up to 100x faster deposition rates with respect to conventional ALD. TNO constructed an S-ALD process toolbox for high throughput ALD on wafers, sheets and foils. Recently, SDBDs were selected to extend the toolbox to plasma enhanced ALD. Implementing an SDBD source in an existing rotary wafer reactor, homogeneous PE-S-ALD was shown for the first time. The operating temperature was reduced down to 80°C allowing deposition on polymer foils. Using plasma in N_2, N_2-O_2 and N_2-H_2, new materials were made like TiN, SiO_2, TiO_2 , InZnO and Ag, so far inaccessible for atmospheric pressure S-ALD.

Contrary to low-pressure plasma, atmospheric plasma tends to filamentary structures (micro-discharges). The past 2 decades, world-wide efforts have been undertaken to improve plasma homogeneity in DBD systems with the electrodes located at both substrate sides and using He gas, short pulses, high frequencies and gas flows. Single-sided SDBD electrode configurations provide remarkably homogeneous and reproducible plasmas in practical gases. Usually the electrical discharge is a mixture of surface glow and micro-discharges, the latter being generated with a sufficient density to reach homogeneous deposition. There is a striking analogy between the saturating charge principle of the planar SDBD and the surface limited surface reaction, as characteristic for ALD processes. Merging both technologies yields the best of two worlds.

As a standard condition, SDBD plasma has been generated parallel and close to the rotating substrate. Obviously, when conductive, semiconductor or highly capacitive substrates are used the SDBD plasma may generate filaments towards the substrate and/or electrostatically interact with electric field sensitive structures. Thus we built various alternative remote SDBD sources minimizing electrical-substrate interaction. For the study of the influence of geometry and flow parameters, thin films were deposited by PE-S-ALD using the different sources.

Also static substrate tests were done with both parallel plasma and remote jet treatments using amorphous C-layer etching to visualize the plasma reactivity and homogeneity. The plasma structures visualized by C-layer transmission show the importance of control of flow and plasma homogeneity. The spatial discharge study is complemented by visual light photography and IR thermography. The experimental data have been validated with a CFD model of plasma species transport yielding a deep understanding of the effects of flow, diffusion and temperature of the SDBD source.

5:00pm **PS+TF-WeA9 Plasma Deposited Barrier Coatings on Plastics: Plasma Characterization and Thin Film Analysis**, ***Peter Awakowicz***, *F. Mitschker*, Ruhr-University Bochum, Germany, *A. Nave*, INP-Greifswald, Germany, *J. Röpcke*, INP-Greifswald, *G. Grundmeier*, Univ. of Paderborn **INVITED**

Thin SiO_2 barrier layers are deposited by microwave plasma enhanced CVD (PECVD). The pulsed mw power is fed in with a plasma line system. In addition, the flat or hollow PET substrates are rf-biased in order to increase film quality and minimize defect density.

Plasma diagnostics is performed with quantitative optical emission spectroscopy (Q-OES) based on a collisional radiative model for nitrogen and confirmed with multipole resonance probe measurements. In addition, nine carbon hydride and carbon oxide species are measured by laser absorption IR measurement while plasma diagnostics is performed.

Analysis of the 30 nm thin films are performed by XPS measurements and defect density measurements. Film porosity is measured with proton exchange measurements and cross linking by looking at the fine structure of the Si 2p peak with highly resolved XPS.

Finally it can be shown that good barrier improvement is realized with the applied deposition method on PET foils and a correlation between plasma parameters and film qualtiy is presented.

5:40pm **PS+TF-WeA11 Flexible, Durable, Self-Cleaning Optical Coatings for Optoelectronics**, ***Thomas Fuerst***, *C.A. Wolden*, Colorado School of Mines

A wide variety of applications such as solar cells, displays, and electrochromics require coatings that manipulate light and provide protective barriers. Silica-titania multilayers have long served as optical components on rigid substrates. Expanding this platform to flexible substrates would allow compatibility with roll-to-roll manufacturing, which would increase manufacturing efficiencies while decreasing costs. Incorporating self-cleaning properties into these coatings would enable longer lifetime, improved efficiency, and reduced maintenance costs for the devices. In this work we describe the design, fabrication, and evaluation of flexible multilayer coating deposited by plasma-enhanced chemical vapor deposition (PECVD) at low temperature. The high and low refractive index materials were TiO_2 and silicone, respectively. PECVD enables the deposition of high quality material at temperatures compatible with polymeric substrates. Silicone is a mechanically robust polymer that imparts flexibility to the coatings and TiO_2 provides UV protection and self-cleaning functionality. The optical stacks were designed using commercial software and validated using UV-Vis-NIR spectrophotometry. The nanoscale control achievable in this process was demonstrated through the fabrication of several Bragg mirrors that were designed to produce blue, green, and red coatings. A five layer broadband anti-reflective (AR) coating was designed and deposited onto a variety of substrates including 1 mm glass, 3 mm FTO-coated glass (TEC-15), flexible polyethylene terephthalate (PET) thin films, and CdTe solar cells built on TEC-15. The absolute transmission of AR-coated glass and PET samples increased by ~5% across the visible spectrum, and solar cells experienced a commensurate boost in efficiency due to improved short circuit density. The multilayer coatings on PET proved to be mechanically robust, as their optical properties remain unchanged after 50,000 cycles of automated bend testing, including both tensile and compressive stress. Lastly, a five layer IR reflector was designed and applied to 1 mm glass and PET. The visible transmittance remained unchanged while the near IR (800-1200 nm) transmission was reduced from 88% to 27% on PET. Studies are underway to assess the long term durability of these coatings to UV exposure and examine the self-cleaning capability through measurements of contact angle and contaminant removal. These results indicate that these nanolaminates show great promise for use in a variety of flexible optoelectronic applications.

6:00pm **PS+TF-WeA12 Microwave Plasma Assisted Chemical Vapor Deposition of High Quality, Single Crystal Diamond Substrates**, ***Shreya Nad***, *Y. Gu*, *J. Asmussen*, Michigan State University

Single crystal diamond (SCD) substrates have very useful properties like their high thermal conductivity, extreme hardness and chemical inertness and are thus deemed to be novel materials for applications in a varied range of fields like high power electronics and X-ray optics. Microwave Plasma Assisted CVD (MPACVD) is one of the most suitable and efficient methods for the synthesis of diamond substrates. MPACVD is carried out in a microwave cavity plasma reactor (MCPR) which consists of a brass cavity to contain the microwave power, a quartz dome and a water cooled substrate holder.

The reactor is first tuned using the 4 length variables to achieve maximum power coupling efficiency. A mixture of methane and hydrogen gasses flows within the quartz dome. The cavity probe excites the plasma at ~ 5 Torr. The plasma discharge is positioned directly above and adjacent to the seed substrate for the growth process to proceed efficiently. Pressure is then gradually increased and depending upon the growth conditions maintained at a high synthesis pressure of 180 – 240 Torr. The substrate temperature is maintained within 1050 – 1150°C for a smooth, high rate growth of SCD. The stable plasma creates a chemically and thermally suitable environment for SCD deposition. The high pressure and high gas temperatures at the core of the plasma discharge break down the methane and hydrogen gas molecules into the important growth radicals. These growth radicals (like CH_3, C_2H_2 etc.) then diffuse through the boundary layer between the plasma and the seed substrate and then deposit on the substrate surface.

The MPACVD method has been used for the growth of both SCDs and polycrystalline diamond (PCD) substrates at high pressures of 160 – 240 Torr, with high growth rates of 20 – 32 µm/hr and for long growth times of 24 – 72 hours. The diamond substrates are then separated from the underlying seed substrate by laser cutting and then the surfaces are mechanically polished for analyses. These substrates have been characterized using FTIR and UV/Vis spectroscopy, SIMS, optical microscopy and X-ray topography. The SCDs grown are of type IIa quality i.e. they have very low nitrogen concentrations of < 100 ppb. They have high transmission even in the low wavelength range. Etch pit density measurements indicate that the substrates grown have low defect density of ~ 10^4 /cm^2.

This presentation describes in detail this efficient deposition process for SCDs and the high quality of the diamond substrates hence achieved.

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 $Cu_xBi_2Se_3$ 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 $Cu_xBi_2Se_3$ 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_2Se_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.

[1] Loth *et al.*, Science **329**, 1628 (2010)

[2] Rau *et al.*, Science **344**, 988 (2014).

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].

[1] M. Yankowitz et al., *Nature Physics* **8**, 382 (2012).

[2] S. Huang et al., arXiv:1504.08357 (2015).

[3] M. Yankowitz et al., *Nano Letters* **15**, 1925 (2015).

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.

Surface Science
Room: 113 - Session SS+AS+EN-WeA

Metals, Alloys & Oxides: Reactivity and Catalysis
Moderator: Daniel Killelea, Loyola University Chicago

2:20pm **SS+AS+EN-WeA1 Understanding Chemical Activity in Pt-Re Bimetallic Systems**, ***Donna Chen***, *R.P. Galhenage, K. Xie, A.S. Duke,* University of South Carolina, *H. Yan*, Brookhaven National Laboratory **INVITED**

The nucleation, growth and chemical activity of bimetallic Pt-Re clusters on titania have been investigated as model systems for understanding Pt-Re catalysts for oxidation reactions. Scanning tunneling microscopy studies demonstrate that exclusively bimetallic clusters can be grown from the sequential deposition of Pt on Re or Re on Pt, provided that the deposition of the first metal creates a high enough cluster density for the nucleation of the second metal. Low energy ion scattering experiments indicate that the bimetallic clusters are Pt-rich regardless of the order of deposition. However, X-ray photoelectron spectroscopy (XPS) suggest that a Pt-Re alloy is formed from deposition of Re on Pt but not from Pt on Re. Furthermore, Re interacts more strongly with the titania support than Pt, resulting in reduction of titania. Temperature programmed desorption studies for CO desorption and methanol reaction confirm that the Re clusters have lower activity than Pt despite their higher surface area, and this behavior is attributed to oxidation of Re by the titania support. The alloyed clusters exhibit new activity for CO and H_2 evolution that is not observed for the pure or unalloyed clusters. Methanol oxidation activity of these model surfaces are studied in a microreactor attached to an ultrahigh vacuum chamber so that the surfaces can be characterized by XPS before and after reaction. Specifically, changes in the oxidation states of Re in the bimetallic and pure Re clusters are investigated.

3:00pm **SS+AS+EN-WeA3 Removal of Surface Carbon from Pt(111) by Hydrogenation via an Ethylidyne Intermediate**, *J.D. Krooswyk, C.M. Kruppe,* ***Michael Trenary***, University of Illinois at Chicago

Transition metals that are used to catalyze reactions of hydrocarbons are often deactivated by the deposition of unreactive carbon on the catalyst surface. The structure and properties of the deposited carbon are often poorly defined. We have investigated the reactivity of carbon deposited onto a Pt(111) surface through exposure to acetylene at 750 K. At this temperature the acetylene is completely dehydrogenated leaving only carbon the surface. Earlier work had shown that the carbon deposited in this way largely consists of C_2 molecules. We have used reflection absorption infrared spectroscopy (RAIRS) to characterize the reactivity of the deposited carbon under ambient pressures of $H_2(g)$ up to 10 torr. The results show that C_2 can be hydrogenated to ethylidyne (CCH_3) and that the ethylidyne is slowly hydrogenated to ethane, which desorbs thus removing carbon from the surface. The maximum coverage of the C_2 molecules can be deduced from comparison with the peak areas measured with RAIRS for ethylidyne formed from ethylene exposure, which is known to give an ethylidyne coverage of 0.25 monolayer. Auger electron spectroscopy confirms that surface carbon is removed by hydrogenation under these conditions. In separate experiments based on comparisons of s- and p-polarized RAIR spectra in which both surface and gas phase species can be simultaneously monitored, we have shown that surface ethylidyne is a spectator species as gas phase acetylene is converted first to gas phase ethylene and then to gas phase ethane. Although ethylidyne is a spectator species in the hydrogenation of ethylene and acetylene to ethane over Pt(111), in the case of C_2 hydrogenation, ethylidyne plays the role of a reaction intermediate.

3:20pm **SS+AS+EN-WeA4 Density Functional Study of the Oxygen Chemistry and NO Oxidation Mechanism on Low-index Surfaces of $SmMn_2O_5$ mullite**, *X. Liu, Z.Z. Chen,* Huazhong University of Science and Technology, China, *K.J. Cho,* The University of Texas at Dallas, *R. Chen,* ***Bin Shan***, Huazhong University of Science and Technology, China

$SmMn_2O_5$ mullite has recently been reported to be a promising alternative to traditional Pt-based catalysts for environmental and energy applications. By performing density functional calculations, we systematically investigated lattice oxygen reactivity and oxygen adsorption/dissociation/migration behaviors on low index surfaces of $SmMn_2O_5$ mullite with different terminations. The (001), (010) and (100)surfaces have lowest barriers against exchanging O species with environments and thus are expected to be active surfaces.Furthermore, we have calculated the reaction routes along different channels on these three surfaces. Our results show that both ER and MvK mechanisms co-exist in NO oxidation by $SmMn_2O_5$. The most active surface is the (010) facet with Mn^{4+} ions in the surface layer where oxidation can be realized by a synergetic mechanism involving ER processes along bridge-MnO channels. The (001) surface with Mn^{4+} ions in the surface layer is also expected to be active for oxidation via the MvK mechanism. On the other hand, despite the low oxygen vacancy formation energy, the (110) surface could easily undergo surface reconstruction and quickly lose active sites. Our calculations also suggest that the rate determining step of oxidation reaction on $SmMn_2O_5$ surfaces is the desorption of NO_2 on both (010) and (001) facets. Our study presents systematic pictures on catalytic activities of $SmMn_2O_5$, which are important to the full understanding and improvement of $SmMn_2O_5$ performance. The comprehensive micro-kinetic model on the reaction dynamics of $SmMn_2O_5$ is under construction.

4:20pm **SS+AS+EN-WeA7 Medard W. Welch Award Lecture - Thermodynamics and Kinetics of Elementary Reaction Steps on Late Transition Metal Catalysts**, ***Charles Campbell****, University of Washington **INVITED**

Experimental and theoretical results concerning the thermodynamics and kinetics of surface chemical reactions of importance in late transition metal catalysis will be reviewed. Topics include: (1) calorimetric measurements of the adsorption energies of small molecules and molecular fragments on single crystal surfaces, and their comparison to different DFT methods; (2) measurements of the entropies of adsorbates and their trends, (3) using these together with elementary-step rate measurements to build microkinetic models for multi-step catalytic reactions, and a method for analyzing these that quantifies the extent to which each elementary step and intermediate controls the net rate; and, (4) measurements of the energies of transition metal atoms in nanoparticle catalysts as a function of particle size and support, which correlate with catalytic activity and sintering rates.

· Work supported by NSF and DOE-OBES Chemical Sciences Division.

5:00pm **SS+AS+EN-WeA9 Bridging Hydroxyl Formation from Water on Reduced $TiO_2(110)$**, ***Nikolay Petrik***, *G.A. Kimmel*, Pacific Northwest National Laboratory

TiO_2 is an important photocatalyst with many practical applications. It is also a good model system for fundamental studies of thermal and non-thermal reactions, including photocatalytic water splitting. Our understanding of water's reactions on TiO_2 surface is limited. In this paper, we have investigated temperature-dependent reaction of water molecules with bridging oxygen vacancy (V_O) on rutile $TiO_2(110)$ surface using three independent methods: i) infrared reflection absorption spectroscopy (IRAS) to monitor the bridging hydroxyl (OH_B or OD_B) formation, ii) electron-stimulated desorption (ESD) of molecular water to monitor the water coverage,[1]and iii) photon-stimulated desorption (PSD) of CO_2 – which is a product of CO photooxidation – to monitor the unoccupied V_O coverage. [2] Narrow, distinct peaks for isolated OD_B and OH_B at ~2736.5 cm^{-1} and ~3711.5 cm^{-1} are detected in P-polarized mode for the samples exposed to D_2O and H_2O, respectively. If water is dosed at low temperature and annealed, bridging hydroxyl peaks appear above 150 K, growing with temperature until ~ 250 K, then saturate. In the same temperature range, molecular water and V_O coverages from the ESD and PSD data decrease in correlated fashion according to the reaction $H_2O_{Ti} + V_O \rightarrow 2OH_B$. The temperature range for this conversion appears to be too broad to be fitted with a single Arrhenius term and a reasonable pre-factor. On the other hand, the data can be fitted well using a "normal" prefactor ($\nu = 10^{12}$ s^{-1}) and a distribution of activation energy (E_a) centered at 0.545 eV with ΔE_a(FWHM) = 0.125 eV. These parameters are close to those obtained from STM data[3] and theory[4] for the water monomer diffusivity on Ti sites, which most likely controls the water – vacancy reaction. This work was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences & Biosciences.

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*** Medard W. Welch Award Winner**

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5:20pm **SS+AS+EN-WeA10 The Adsorption and Desorption of Small Hydrocarbons on Rutile TiO_2(110)**, ***Long Chen***, *R.S. Smith, B.D. Kay, Z. Dohnalek*, Pacific Northwest National Laboratory

The interaction of small hydrocarbons with metal and metal oxide surfaces is important for a wide range of applications including heterogeneous catalysis, atmospheric chemistry, geochemistry and chemical sensing. In this work, temperature programmed desorption (TPD) and molecular beam techniques are used to study the adsorption and desorption kinetics of small hydrocarbons (C_1 - C_4) on rutile TiO_2(110) surface. In addition to n-alkanes, 1-alkenes (ethylene, propylene and 1-butylene) and 1-alkynes (acetylene, propyne and 1-butyne) were included to follow the effect of the nature of the carbon-carbon bond on hydrocarbon binding. We show that the sticking coefficients for all the hydrocarbons studied here are close to unity (> 0.95) at an adsorption temperature of 60 K. Similar to previous studies on metal and metal oxide surfaces, for n-alkanes on TiO_2(110) we find a linear increase in desorption energy with chain length. In contrast, for 1-alkenes and 1-alkynes, a roughly linear relationship between desorption energy and chain length is also observed at low coverages, but with a much smaller slope, suggesting that the additional CH_x segments either interact less efficiently with the substrate or destabilize the bonding of the unsaturated carbon-carbon bond. Further, we also determined the absolute saturation coverages of each hydrocarbon on the five-fold coordinated titanium sites (Ti_{5c}). We show that except for CH_4, the saturation coverages of the same type of hydrocarbons on Ti_{5c} sites are nearly independent of the chain length, and that the saturation coverages of 1-alkynes consistently exceed those of n-alkanes and 1-alkenes, contrary to what one would expect based on their sizes.

5:40pm **SS+AS+EN-WeA11 Pd-Au *Single Atom Alloys* for the Activation of Diatomic Molecules**, ***Felicia Lucci***, *E.C.H. Sykes*, Tufts University Department of Chemistry

Pd-Au alloys are known to catalyze a wide range of hydrogenation and oxidation reactions; however, the size of Pd ensembles in Au required for small molecule activation is not well understood. On the atomic scale, we investigate size effects of Pd atoms in Au for the catalytic activation of H_2 and O_2. We show that isolated Pd atoms are capable of catalyzing the dissociative adsorption of H_2, a process which was previously thought to require contiguous Pd sites. H spillover from active Pd sites to the Au surface can be induced the adsorption of CO. Conversely, single Pd atoms are not capable of O_2 dissociation. Small Pd clusters on Au enable O_2 activation and adsorption at Pd-Au interface sites. Since weakly bound H and O atoms are capable of enhancing reaction selectivity on Au substrates, this Pd-Au system serves as an ideal model system with which to probe selective hydrogenation and oxidation reactions at both single and ensemble active sites.

6:00pm **SS+AS+EN-WeA12 Pt/Cu Single Atom Alloys for Highly Selective Formic Acid Dehydrogenation**, ***Matthew Marcinkowski***, *C.J. Murphy, M.L. Liriano, N.A. Wasio, F.R. Lucci, E.C.H. Sykes*, Tufts University Department of Chemistry

Selective decomposition on metal catalysts is a critical step in formic acid's application as a hydrogen storage molecule and for its use in direct formic acid fuel cells. Depending on the metal, formic acid can decompose via a dehydrogenation pathway to produce CO_2 and H_2, or a dehydration pathway to produce CO and H_2O. For most applications, very high selectivity to dehydrogenation is preferred as reactively formed CO from dehydration can poison the catalyst. The Cu(110) surface is known to selectively decompose formic acid via dehydrogenation, however, despite being the most dominate facet of nanoparticles, Cu(111) has received little study. Pt surfaces exhibit greater reactivity to decomposition, but are not as selective resulting in increased catalyst poisoning. We report that formic acid on Cu(111) and Pt/Cu(111) selectively decomposes via dehydrogenation. We find the bare Cu(111) surface to be 100% selective towards dehydrogenation, but not very active. Substitution of 1% of a monolayer of Pt into the Cu(111) surface results in a single atom alloy (SAA) that maintains this high selectivity and is ~six times more reactive than Cu(111). Higher coverages of Pt improve reactivity further, but beyond the single atom regime the selectivity towards dehydrogenation decreases and dehydration is observed. Our results show that Pt/Cu SAAs significantly improve the reactivity of Cu, while also maintaining high selectivity towards dehydrogenation, therefore avoiding catalyst poisoning by CO. Based on our results, real nanoparticle catalysts designed on the SAA principle are expected to be promising candidates for formic acid dehydrogenation.

Surface Science
Room: 112 - Session SS+AS-WeA

Surface Dynamics, Non-Adiabaticity, and Single Molecule Phenomena
Moderator: Eddy Tysoe, University of Wisconsin-Milwaukee

2:20pm **SS+AS-WeA1 Benchmarking Theory with Vibrational State Resolved Reactivity Measurements**, ***Arthur Utz***, *E. Peterson, E. Dombrowski, E. Nicotera, E. High*, Tufts University

Electronic structure calculations provide predictions of energy thresholds for a wide range of surface chemical reactions, and they are the basis for significant advances in our understanding of surface reactivity. Despite the central role these calculations and their predictions play, testing the absolute accuracy of these calculations with direct experimental measurements has proven to be challenging.

The presentation will focus on using the results of state-resolved beam-surface scattering measurements to benchmark theoretical predictions. We find that when these measurements are performed on a cold surface, we observe sharp energetic thresholds for reaction. These observations result from our ability to control and vary precisely all energetic degrees of the system. These experimentally measured threshold energies can be compared directly with both electronic structure calculations, as well as with quantum dynamics predictions of chemical reactivity. We will compare experimental results for methane dissociation on Ni(111) with recent computational predictions from the Jackson group to illustrate this approach. We will also provide an update on our work extending this approach to other molecule-surface systems.

2:40pm **SS+AS-WeA2 Confirming the role of Hydrogen Bonding in Electron-promoted Desorption at Water Ice Surfaces.**, *D. Marchione, A.G.M. Abdulgalil, M.P. Collings,* ***Martin McCoustra***, Heriot-Watt University, UK

We have previously reported observations of large ($>10^{-16}$ cm^2), low-energy (<500 eV), electron-promoted desorption cross-sections for benzene (C_6H_6) molecules adsorbed on the surface of amorphous solid water [1]. We will now report on the extension of this work to other molecular solids exhibiting varying degrees of hydrogen bonding within the molecular solid itself and between the solid surface and adsorbed benzene; specifically we have repeated our measurements employing substrates comprised of solid methanol (CH_3OH) and diethyl ether ($CH_3CH_2OCH_2CH_3$). Our report will detail our studies of the structure of adsorbed layers of C_6H_6 on the molecular solids and demonstrate the crucial role of hydrogen bonding in propagating electronic excitation to the solid-vacuum interface where C_6H_6 desorption can occur. Competitive electron-promoted chemistry in the form of H_2 formation will also be reported. Conclusions related to the impact of these observations on the early phase of icy interstellar grain chemistry will be discussed.

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3:00pm **SS+AS-WeA3 Strategic Applications of the Vibrational Dynamics of the Outer Layer of Metal Nanoparticles**, ***Marisol Alcantara Ortigoza***, University of Central Florida **INVITED**

The structure characterization, stability and thermal properties of nanoparticles (NPs) are topics of fundamental and technological significance. This information, however, is not always readily available from experiment. Moreover, the vibrational density of states VDOS of small (<2 nm) metal NPs definitely does not have a quadratic decay at the low-frequency end, for which the thermal properties cannot be obtained from the VDOS as Debye proposed in 1912. The features particular to the VDOS of NPs will be rationalized in terms of the charge density distribution around low-coordinated atoms, the quasi-radial geometric distribution of NPs, force constant variations, degree of symmetry of the nanoparticle, discreteness of the spectrum, and the confinement of the eigenmodes. I will present an explanation and application of the enhanced low- and high energy tails of the vibrational density of states (VDOS) of nanoparticles with respect to their bulk counterparts, as well as show that the eigenmodes defining the two extremes of the VDOS are not that alien to widely studied surface phonons. I will show that the high- and low-energy tails of the VDOS of NPs may be a powerful tool to reveal information about their chemical composition and geometric structure of small NPs. For example, the size of the confinement gap at the low-frequency end of the VDOS and the extent by which the high-frequency end surpasses the bulk limit may indicate whether a NP is bulk-like or non-bulk-like and the extent to which it is disordered or segregated. Regarding thermal properties, I will also show that for NPs with a largely discrete VDOS, the frequency of their fundamental mode may largely determine their thermal properties.

4:20pm **SS+AS-WeA7 An Accurate Full-Dimensional Potential Energy Surface for H at Au(111): The Importance of Nonadiabatic Electronic Excitation in Energy Transfer and Adsorption**, *S.M. Janke, A. Kandratsenka,* ***Daniel Auerbach****, A.M. Wodtke*, Max Planck Institute for Biophysical Chemistry, Germany

We have constructed a potential energy surface (PES) for H atoms interacting with *fcc* gold based on the form of the PES in Effective Medium Theory. The PES was adjusted to match energies calculated by DFT in many configurations, including many with the Au atoms displaced from their lattice positions. It describes both the interatomic forces and electron densities in *full dimension* with the accuracy of the *ab initio* energies used in its construction. Calculations describing the motion of H and Au atoms using this full dimensional adiabatic PES agree with results obtained previously using Ab Initio Molecular Dynamics, demonstrating the accuracy of the PES for configurations occurring in the scattering of H atoms from a surface at finite temperature.

The analytic expression for the total energy contains the embedded electron density leading to a self-consistent approach to simulating nonadiabatic trajectories. We find that nonadiabatic electron-hole pair excitation is the most important energy loss pathway for the H atom. The calculated energy distributions for scattered H atoms are in reasonable agreement with experimental results that are just becoming available. and determines the probability and mechanism for its adsorption. Analysis of trajectories calculated with and without nonadiabatic energy dissipation shows the adsorption or sticking probability as well as the mechanism of H atom adsorption is changed dramatically by nonadiabatic energy transfer

4:40pm **SS+AS-WeA8 STM Characterization of Quasi-one Dimensional C_{60} Nanostructures on Rippled Graphene**, *C. Chen, H. Zheng, A. Mills,* ***Chenggang Tao***, Virginia Tech

Highly ordered one-dimensional (1D) molecular configurations are excellent model systems and prototypes of 1D quantum confinement of electronic states, and thus have potential importance in electronic nanodevices, spintronics and solid-state quantum computation. Due to the spherical geometry of C_{60} molecules, it has been challenging to experimentally realize quasi-1D C_{60} nanostructures, a highly anisotropic configuration. We will present our recent scanning tunneling microscopy (STM) characterization of novel quasi-1D C_{60} nanostructures on rippled graphene. Through careful control of the subtle balance between the linear periodic potential of rippled graphene and the C_{60} surface mobility, C_{60} molecules can be arranged into a 1D C_{60} chain structure with widths of two to three molecules. At a higher annealing temperature, the chain structure transitions to a more compact hexagonal close packed quasi-1D stripe structure. We will also discuss our scanning tunneling spectroscopy (STS) measurements on this hybrid system.

5:00pm **SS+AS-WeA9 Classical and Quantum Description of Ion Desorption from Ionic Crystals**, ***Leszek Markowski***, University of Wroclaw, Poland

It is well known that irradiation of the solid with electrons or photons can cause its decomposition. This process, or, more adequately processes, is very fast (typically finalized within a time shorter than 10^{-14} s) and is realized mainly by desorption of atoms or ions.Unfortunately, until now, existing models still do not give a proper value of the desorption yield and, simultaneously, a correct kinetic-energy distribution of emitted particles, as compared to the experimental observations.

In this talk a classical, quasi-quantum and quantum description of the positive ion desorption from ionic crystal surface, in which three potentials are involved, will be discussed and compared. It will be shown that the quantum description allows to explain some effects observed experimentally, such as a periodicity of small oscillations on the kinetic energy distribution (KED) curves (predicted by Wave-Packet Squeezing model) and emission through a temporarily existing potential barrier from the temporary bounded states located above the vacuum level. Moreover, analysis method of the ion KED oscillation and the fitting procedure which allows to determined a final effective desorption potential will be presented.

For two examples discussed, Li^+ desorption from LiF and Na^+ desorption from NaCl, desorption from two desorption sites can be distinguished – dominating ion desorption channel from adatom sites (more than 95%) and marginal one from the sites in the first surface layer. For the second desorption channel neighboring negative ions, due to surface relaxation lying in the first surface layer slightly above positive one, can act as a two-dimensional array of rosette-like apertures. In consequence, positive ions after passing through them may form diffraction pattern.

Finally, it appears that when desorption process is described using three potentials both the ions desorption efficiency and their kinetic-energy distribution are in agreement with the experimental results.

5:20pm **SS+AS-WeA10 Spin and Isotope Effects on Molecular-Hydrogen Adsorption on Pd(210)**, *H. Kobayashi, S. Ohno, M. Wilde,* University of Tokyo, Japan, *M. Matsumoto,* Tokyo Gakugei University, Japan, *S. Ogura,* ***Katsuyuki Fukutani***, University of Tokyo, Japan

Molecular hydrogen is physisorbed on flat metal surfaces via van der Waals interaction. By taking advantage of the fact that molecular hydrogen exists in nuclear-spin isomers of ortho and para species [1], we have shown the interaction potential on Ag(111) is anisotropic with a slight perpendicular preference [2]. The Pd(210) surface has a step-like structure consisting of alternately aligned (100) and (110) terraces, and it has been shown that H_2 is rather strongly adsorbed on H-covered Pd(210) with a significant contribution of orbital hybridization [3]. On the other hand, it has been suggested that molecularly adsorbed species could be important for hydrogen absorption into the interior of Pd surfaces [4]. In the present study, we have investigated the adsorption of H_2 and D_2 on the Pd(210) with temperature-programmed desorption (TPD) combined with resonance-enhanced multi-photon ionization (REMPI).

When Pd(210) was exposed to H_2 at 115 K, TPD revealed a desorption peak at 180 K (α-peak) originating from the absorbed state as well as a peak at 280-320 K (b-peak) due to chemisorbed H. From the uptake rate of the α-peak, the absorption probability of H on Pd(210) was estimated to be 3×10^{-3}. When the surface was exposed to either H_2 or D_2 at 45 K, on the other hand, an additional TPD peak was observed at about 70 K (γ-peak), which was attributed to molecular adsorption. While a small difference between H_2 and D_2 was observed for the b-peak, the γ-peak temperature of D_2 was found to be higher than that of H_2 by 9 K, which corresponds to the difference in the adsorption energy of about 20 meV. Assuming that this difference is due to the zero-point energy difference in the adsorption potential, the adsorption potential was analyzed in terms of the Morse potential. By applying REMPI-TPD, furthermore, the TPD spectra of ortho-H_2 in the rotational state of J=1 and para-H_2 in J=0 were state-selectively measured. The desorption temperature of ortho-H_2 was found to be higher than that of para-H_2 by about 4 K, which corresponds to a difference in the adsorption energy of about 10 meV. We discuss that this large energy difference between the ortho and para species originates from the potential anisotropy on the basis of the first-order perturbation.

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[3] P. K. Schmidt et al., Phys. Rev. Lett. 24 87, 096103 (2001).

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5:40pm **SS+AS-WeA11 Eley-Rideal Typed Mechanism of Formate Synthesis by Hydrogenation of Carbon Dioxide on Cu Surfaces**, *J. Quan,* University of Tsukuba, Japan, *T. Ogawa,* Universityy of Tsukuba, Japan, *T. Kondo,* University of Tsukuba, Japan, *G. Wang,* Nankai University, China, ***Junji Nakamura***, Univerisity of Tsukuba and ACT-C, Japan

Methanol synthesis by hydrogenation of CO_2 using Cu catalysts is one of the promising reactions to convert CO_2 into useful chemicals. Formate species is the pivotal intermediates formed as the initial step of CO_2 hydrogenation ($CO_2 + H_a \rightarrow HCOO_a$). The reaction rate of formate synthesis is very low and the reaction probabilities are about 10^{-12} at 340K. Our previous kinetic measurements have suggested that formate is synthesized via Eley-Rideal typed mechanism, in which CO_2 molecules directly attack adsorbed hydrogen atoms on Cu surfaces. The structure insensitivity observed for formate synthesis experiments on Cu(111), Cu(100), and Cu(110) were well explained by the Eley -Rideal mechanism based on DFT calculations. In addition, sharp angular desorptions of CO_2 have been observed for formate decomposition as the reverse reaction of formate synthesis, indicating thermal non- equilibrium reaction. In the present study, we performed molecular beam experiments to prove the Eley-Rideal typed mechanism, in which CO_2 molecules with controlling vibrational and translational energies were reacted with adsorbed hydrogen on cold Cu(111) and Cu(110) surfaces (T_S =150-215 K). We confirmed the formation of formate species on Cu(111) and Cu(110) with reaction probabilities of 10^{-5} by heating nozzle above 1000 K, while no formate is formed at nozzle temperatures below 1000 K. The results indicate the Eley-Rideal typed mechanism with thermal non-equilibrium character. DFT calculations also reproduce the Eley-Rideal typed mechanism, in which vibrational excitations of CO_2 are required to overcome the barrier of formate synthesis.

Thin Film
Room: 114 - Session TF+AS+BI-WeA

Thin Films for Biological and Biomedical Applications
Moderator: Christophe Vallee, LTM, Univ. Grenoble Alpes, CEA-LETI, Angel Yanguas-Gil, Argonne National Lab

2:20pm **TF+AS+BI-WeA1 On-chip Characterization of Engineered Nanomaterial Surface Properties by Real-time Affinity Monitoring**, *C. Desmet, A. Valsesia, P. Colpo,* European Commission, Joint Research Centre (JRC), ***Francois Rossi***, European Commission, Joint Research Centre (JRC), Italy **INVITED**

The exhaustive characterization of the physico-chemical properties of engineered nanomaterials (ENMs) is essential to understand their mode of action and potential impact on health and environment. The development of characterization methods has been the object of important work in the past years, and has led to a better understanding on the ENM interaction with cellular systems and living organisms. One of the important surface properties of ENMs is the surface energy, for which there is no standard characterization technique established. Here, we demonstrate the feasibility of a characterization method based on a disposable microfluidic chip connected to an optical reader. The detection platform is based on the use of a micropatterned surface with tuned surface properties to bind ENMs selectively by hydrophobic forces and electrostatic interactions. The real-time absorption of ENMs on the differently functionalized micro domains is monitored by a microscope-coupled camera and gives information on the kinetics of adsorption, related to the affinity of the ENMs for the different surfaces as a function of their sizes and shapes. Interpretation of the results within the extended DLVO theory allows retrieving the surface energy characteristics of the ENMs surfaces. The key advantage of the device is the increase of the characterization throughput thanks to the all-in-one characterization process and the multiplexing that is able to replace the use of different methods and expensive equipment. In this way, the full characterization of ENMs could be expanded in all the areas covering nanomaterial-related applications.

4:20pm **TF+AS+BI-WeA7 Titanium-Niobium Thin Films Deposited by Magnetron Sputtering on AISI 316L Stainless Steel Substrate**, *D. Gonzalez, T.C. Niemeyer, C.R.M. Afonso,* ***Pedro Nascente***, Federal University of Sao Carlos, Brazil

Metallic biomaterials such as AISI 316L stainless steel (SS), chromium-cobalt alloys, titanium and its alloys are commonly used in medical implants due to their interesting mechanical properties and thermal stability. However, 316L SS and Cr-Co alloys have much higher elastic modulus than bone, causing the loss after some years of implantation [1]. The elastic modulus of Ti-based alloys ranges from 55 to 110 GPa, being significantly lower than those for 316L SS (210 GPa) and Cr-Co alloys (240 GPa), making them more suitable for use in dental and orthopedic applications. Also Ti alloys present high strength, low density, high corrosion resistance, and good biocompatibility [1]. Pure Ti has two allotropic forms: hexagonal closest-packed (hcp), known as α phase, and body centered cubic (bcc), known as β phase, structures. Studies have shown that the addition of alloying β-stabilizing elements such as V, Mo, Nb, Zr, Mo, and Ta causes the decreasing of the modulus of elasticity of the β-Ti alloys without compromising the strength [1]. In this study, thin films of Ti-Nb alloys were deposited on AISI 316L stainless steel substrate by magnetron sputtering, and the structure, morphology, and composition of the films were analyzed by means of X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). Thin films of three compositions were produced: $Ti_{85}Nb_{15}$ (Ti-26wt% Nb), $Ti_{80}Nb_{20}$ (Ti-33wt% Nb), and $Ti_{70}Nb_{30}$ (Ti-45wt% Nb). Structural characterization by XRD indicated that only the β phase was present in the thin films. XPS analysis showed a predominance of oxidized Ti and Nb on the film surfaces. TEM analyses were carried out in the following image modes: bright field (BF) images, selected area diffraction (SAD), scanning mode (STEM) BF and in annular dark field (ADF), and X-ray mapping using energy dispersive spectroscopy (EDS). For the $Ti_{80}Nb_{20}$ alloy film, TEM analysis showed columnar grains (~100 nm width) of -Ti phase, with a Nb-rich transition layer ranging from finer grains (in contact with SS substrate) to a coarser columnar grains. For the $Ti_{75}Nb_{25}$ alloy film, TEM analysis showed columnar grains (~50 nm width) of β-Ti phase, with a transition layer away from the SS substrate.

Acknowledgements: A.L. Gobbi, C.A. Silva, S.R. Araujo, and J. Bettini from the Brazilian Nanotechnology National Laboratory, for their assistance in the growth and characterization of the thin films; and CNPq and CNPEM (Brazil), for support.

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4:40pm **TF+AS+BI-WeA8 SAM-based Models of Cell Surfaces to Study the Interactions with Lectins and Bacterial Fimbriae**, ***Andreas Terfort***, University of Frankfurt, Germany, *K. Lindhorst*, University of Kiel, Germany

Biologically important events such as cell-cell adhesion or infection typically start by directed and selective interactions with the highly glycosylated layer surrounding most eukaryotic cells. This layer, called the glycocalyx, consists of intricate glycopolymers, which – although in apparent disorder – clearly identify the cells. It is therefore of paramount interest to understand, which structural elements are important for the cell identification.

Self-assembled monolayers (SAM) can be used to simulate the chemical and sterical environment within such a glycocalyx. For this, glycosides are attached to oligoethyleneglycol (OEG) chains, which simulate the hydrogel matrix for the respective receptor. In this talk, we will focus on mannose-derivatives, which can be selectively recognized either by a lectin, concanvalin A, or by the adhesive fimbriae (tiny protein extrusions) of E. coli cells.

We would like to present different strategies for the construction of such SAMs [1,2] and discuss the advantages and disadvantages of these approaches. In extension of the mostly static systems, we will also present an approach to dynamically reorient the glycoside at the interface to determine the influence of steric factors on surface recognition [3].

References

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5:00pm **TF+AS+BI-WeA9 Improving the Long-Term Stability of Thin-Film Contact and Electrode Metallizations for Implantable Silicon Neural Interfaces**, ***Brian Baker***, *R. Caldwell*, University of Utah, *H. Mandal*, Blackrock Microsystems, *R. Sharma, P. Tathireddy, L.W. Rieth*, University of Utah

The Utah Electrode Array (UEA) is a penetrating multi-electrode interface designed to be implanted and communicate directly with the brain and peripheral nerves through recording and stimulation. These devices are used for treating neural disorders and controlling prosthetics.

The UEA is micromachined out of single crystal silicon and uses a Pt/Ir/IrOx thin film metallization stack as an electrical interface on the electrode tip and a Pt/Ir/Pt stack on the backside contacts. Delamination of these thin metal layers has been observed during fabrication processes, soak testing, and in vivo operation, and is the critical failure mode examined in this study.

Db-FIB and Cross-sectional STEM analysis were used to identify Kirkendall voids as the root cause of the adhesion failures. This investigation showed that these voids form during the platinum silicide annealing process at the interface between the PtSi and the Ir layers.

Typical thicknesses of the UEA metallization are 200 nm/500 nm/520 nm Pt/Ir/IrOx, and 200 nm/200 nm/325 nm Pt/Ir/Pt. We report the results of replacing the 200 nm base layer with 1) a 25 nm Pt base layer or 2) a 50 nm co-sputtered PtSi base layer. These layers were subjected to typical UEA annealing conditions of 375 °C in forming gas for 45 minutes, followed by a 475 °C, 30 minute oxygen anneal.

Cross-sectional STEM elemental mapping of each film stack showed complete transformation of the platinum layer to PtSi, with a 40 nm layer of iridium silicide formed at the PtSi/Ir interface. In addition, a a reduction in the nanogaps caused by Kirkendall voiding was demonstrated by STEM analysis in the two new film stacks.

Both the 25 nm Pt base layer stack and the 50 nm co-sputtered PtSi base layer stack demonstrate low-resistance Ohmic contacts and wire bondability after annealing. Further electrical characterization of these thinner base layer stacks used on tip metal demonstrated impedances of 5-10 kOhms and charge injection capacities of 1-2 mC/cm^2 for typical electrode tip surface areas. Cross-sectional STEM analysis of the reactively sputtered iridium oxide film reveals a three dimensional morphology whose nanostructures provide a large augmentation of electrode surface area and a corresponding increase in charge injection capacity. In vitro stimulation and accelerated lifetime tests are ongoing and electrical measurements and thin film adhesion stability will be reported.

5:20pm **TF+AS+BI-WeA10 On-Surface Synthesis of Organic Nanostructures on Copper Surfaces**, *Q.T. Fan,* University of Science and Technology of China*, J.M. Gottfried,* Philipps-Universität Marburg, Germany*, **Junfa Zhu***, University of Science and Technology of China

The on-surface synthesis of organic nanostructures known as bottom-up approach paves a new way for surface structuring, which plays a vital role in catalysis, sensor systems, or organic electronics. In this presentation, we will report our recent studies on the on-surface synthesis of 2D organic nanostructures on Cu(111) and Cu(110) surfaces using a specially designed bromo-terphenyl precursor, namely 4,4''-dibromo-*meta*-terphenyl (DMTP). The study was performed under ultra-high vacuum conditions using a combination of scanning tunneling microcopy (STM) and X-ray photoelectron spectroscopy (XPS). The results indicate that the two different surface structures of Cu drive the precursor molecule to form different nanostructures on the surface. We will show temperature-dependent organic nanostructures formed after DMTP adsorbed on Cu(111) and Cu(110). These organic nanostructures include large-area, defect-free 2D ordered nonostructures of intact DMTP on Cu(111), 1- or 2D polymeric zigzag organometallic intermediates formed on Cu(111) and Cu(110), and the macromolecular nonostructures including hexagonal close-packed arrays of cyclo-octadecaphenylene (hyperbenzene), oligophenylene nanowires formed through Ullmann reaction mechanism. *This work is supported by the National Natural Science Foundation of China (21173200,* 21473178*) and National Basic Research Program of China (*2013CB834605*)*

5:40pm **TF+AS+BI-WeA11 Carbon Nanotube-Templated, Porous Films for Thermal Isolation**, *J.M. Lund, D.B. Syme, R. Vanfleet, R.C. Davis, B.D. Jensen, **Brian Iverson***, Brigham Young University

Sensor usage has increased dramatically in detection applications due to miniaturization of components through micro and nanofabrication. These fabrication methods have also greatly increased production rates, as several sensors can be constructed in parallel. Reduction in feature size of sensors has resulted in an increase in sensor component proximity, making thermal diffusion or cross talk detrimental to proper function. This work investigates the use of carbon nanotube-templated manufacturing (CNT-M) to create thin-film, isolation layers for use in thermal sensors. CNT-M is a process wherein carbon nanotubes are used as a scaffold and coated with insulating materials (e.g. SiO_2) to create porous insulating films. Carbon nanotubes are removed in a post-deposition, burn out process rendering a porous matrix of insulating material. Thin-films are characterized using scanning electron microscopy, nanoindentation and the 3-omega method to determine mechanical and thermal properties. Thermal conductivity on the order of air has been observed while still maintaining a rigid structure that is compatible with subsequent MEMS processing.

Thin Film
Room: 111 - Session TF+AS+EM+EN+MN-WeA

CV Infiltration Methods and Energetic and Thermal Properties of Thin Films

Moderator: Richard Vanfleet, Brigham Young University, David Allred, Brigham Young University

2:20pm **TF+AS+EM+EN+MN-WeA1 The Many Avatars of PVD**, ***Murali Narasimhan***, Applied Materials, Inc. **INVITED**

Physical Vapor Deposition has been used for many years for depositing thin film coatings for diverse uses ranging from jewelry to industrial cutting tools. PVD has found usage in the manufacture of advanced semiconductor manufacturing for depositing various metals and some specialty dielectrics as well. The majority of high purity metal deposition for semiconductor use has been done using PVD although the use of CVD and ALD has increased over the years because of requirements of conformality and gap fill where conventional planar PVD has not been adequate. However, breakthroughs in PVD technology have been successful in extending the use of PVD to advanced semiconductor manufacturing nodes by changing the geometry of PVD sources and reactors and the nature of the plasma involved. Collimated and long-throw sources developed by the semiconductor equipment industry in the early '90s enabled the deposition of high-purity Ti to lower contact resistance for transistors. Reactive sputtering of TiN enabled a robust barrier for CVD W plugs used at the 0.5um node. Further, use of electromagnetic fields to ionize and then guide the plasma and sputtered ionized atoms has been successful in improving the conformality of PVD Ti films. Ionized Metal Plasma (IMP), Hollow-Cathode Magnetron (HCM) and Self-Ionized Plasma (SIP) were innovations in ionized PVD reactor design that led to widespread adoption of PVD TaN and PVD Cu for Cu interconnect barrier and seed layer production from the 90nm node to the present. The application of thermal energy on the substrate during PVD Al and Cu has been useful in improving the flow of deposited material and subsequent gap-fill of sub-micron features. The use of Radio Frequency (RF) energy to power the target has allowed for more efficient ionization at lower power levels. The application of a capacitive tuner to modulate the ion bombardment on the wafer and tailor the film properties of TiN for hard mask applications has enabled the realization of etched features at the 22nm node. Pulsed DC magnetrons enable sputtering of dielectric materials, thus opening up the controlled deposition of thin films of insulating films for various applications such as improving the brightness of high-efficiency LEDs. Multi-cathode off-axis PVD magnetrons have enabled the deposition of multi-layers of ultra-thin films for magnetic devices such as advanced in-plane and out-of plane MRAM and the manufacture of EUV mask blanks for sub 10nm manufacturing. This talk will present the above listed progression of PVD technology over the years and its use for many applications in semiconductor manufacturing.

3:00pm **TF+AS+EM+EN+MN-WeA3 Reactive Foil Ignition by Laser Irradiation: Experimental and Modeling Results**, ***Ryan Murphy****, C.D. Yarrington,* Sandia National Laboratories*, R.V. Reeves,* Lawrence Livermore National Laboratory*, D.P. Adams*, Sandia National Laboratories

It has been shown that forced mixing of reactive layers (foils) leads to an exothermic release of energy after initiation by pulsed laser irradiation. In order to understand the ignition of foils initiated by laser irradiation, we study the interaction of laser pulses with Al/Pt multilayer reactive foils prepared by sputter deposition. It will be shown that the single-pulse ignition threshold and dynamics are dependent on the length of the laser pulse as the pulse length is varied from 150 fs to 100 ms. The dependence of the ignition threshold on pulse length is a combination of laser-material interactions such as the size of the heat affected zone and the onset of ablation for ultrafast irradiation. Simulations of single-pulse laser heating were performed with Aria, the thermal package of the SIERRA finite element computational framework. Three-dimensional geometries were subjected to laser flux boundary conditions equal to those measured from the experimental conditions. Modeling and experimental results are correlated to show the effects of the heat affected zone size and shape on ignition thresholds and onset times.

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3:20pm **TF+AS+EM+EN+MN-WeA4 The Effects of a Heat Sink on Self-Sustained Propagating Reactions in Sputter-Deposited Bimetallic Multilayers**, ***David Adams****, R.V. Reeves, M. Hobbs*, Sandia National Laboratories

Reactive multilayers grown by sputter deposition have recently attracted interest for applications including material joining (soldering, brazing) and energy sources. For these applications, a metal-metal multilayer is typically designed to have many discrete reactant layers and a composition that corresponds to the peak enthalpy for a given material system. A thickness of reactive multilayers as small as 1.6 microns has recently been demonstrated for microelectronics joining (Braeuer et al. ECS Transactions, 2012). However, little is known about the minimal multilayer thickness required for ensuring a self-sustained, high temperature synthesis (SHS) reaction.

With this presentation, we describe the behavior of thin reactive Al/Pt multilayers tested as freestanding foils and as adhered films. For multilayers having a total thickness of 1.6 microns, self-sustained, high temperature reactions readily occur when the multilayer is tested as a freestanding foil. When coupled to a semi-infinite substrate, the likelihood of reaction is reduced depending on the multilayer design.

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5:00pm **TF+AS+EM+EN+MN-WeA9 Beyond Deep Silicon Etching – Generating High Aspect Ratio Microstructures by Infiltration of Carbon Nanotube Frameworks**, ***Robert Davis***, Brigham Young University **INVITED**

In addition to being the anchor material for microelectronics, silicon is widely used as the basis of high aspect ratio microfabrication for MEMS with applications ranging from inertial sensors to neural probe arrays. Carbon nanotube templated microfabrication (CNT-M), extends the palate of materials and structures for high aspect ratio microfabrication beyond those achievable with vertically etched bulk silicon. In CNT-M, 3-D forests of patterned vertically-aligned carbon nanotubes are grown as a high aspect ratio framework and then the "forests" are infiltrated with a secondary material by chemical vapor deposition. Precision structures (including nanoporous structures) with very high aspect ratios (greater than 400:1) can be generated with CNT-M. The infiltration materials range from ceramics to metals and include silicon dioxide, silicon nitride, carbon, nickel, and yes silicon. We are using CNT-M to fabricate functional structures for applications including mechanical actuation, chemical separations and detection, and electrochemical energy storage.

5:40pm **TF+AS+EM+EN+MN-WeA11 The Influence of Thin Binder Films on Reaction Behavior in Reactive Powder Complexes**, ***Robert Reeves***, *K.T. Sullivan, A.E. Gash*, Lawrence Livermore National Laboratory

With the recently renewed interest in additive manufacturing (AM), there has been a recent upswell in the number of AM processes available. One such process that could be useful for reactive materials utilizes a curable liquid binder to adhere loose powders into coherent solid forms. In this process, tap-density powders are nearly saturated with binder, so the resulting film of binder present on each particle can represent a significant contaminant to the reaction system. In this work, the effect of the binder on reaction behavior in the Ni-Al system is explored. First, the distribution of binder and its elemental constituents are studied by electron microscopy and energy dispersive spectroscopy for powders with varying levels of binder saturation. Then, the effect of binder on the reaction kinetics and overall behavior is investigated. The change in overall heat release and apparent activation energy are quantified through differential scanning calorimetry, and the bulk reaction propagation rate is measured by high speed photography as a function of the weight fraction of binder in the compact. Finally, the reaction products are identified through x-ray diffraction. In all tests, comparisons are made to the neat Ni-Al system.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

6:00pm **TF+AS+EM+EN+MN-WeA12 Carbon Nanotube Sheets from Horizontally Aligned Carbon Nanotubes**, ***Nathan Boyer***, *D.B. Syme, J.T. Rowley,* Brigham Young University*, M. Harker, R. Creighton, S. Cornaby,* Moxtek Inc.*, R. Vanfleet, B.D. Iverson,* Brigham Young University*, L. Pei,* Johns Hopkins University*, R.C. Davis*, Brigham Young University

Carbon sheets comprised of horizontally aligned carbon nanotubes (CNT) were prepared by rolling vertically aligned CNTs into a thin-film. A subsequent infiltration step to coat the rolled CNTs with amorphous carbon or polymer has also been performed to improve adhesion of neighboring CNTs. Amorphous carbon infiltration was achieved using chemical vapor deposition and polymer infiltration was performed by dipping the sheet into a solvent-mediated, polymer solution. The typical failure mode of the CNT thin-films is to tear parallel to the alignment of the CNTs. Infiltration of the aligned CNT film with additional materials strengthens the film against tearing and increases burst pressure. Non-infiltrated CNT thin-films have sustained a differential pressure of 1.4 atm over a circular area of 7 mm2 on a bulge test apparatus. Both carbon and polymer infiltrated sheets could be used in many applications including micromechanical sensing and actuation.

Vacuum Technology
Room: 230B - Session VT-WeA

Vacuum Quality and Partial Pressure Analysis
Moderator: Steve Borichevsky, AMAT VSE, Ted Martinez, SLAC National Accelerator Laboratory

2:20pm **VT-WeA1 Plasma Cleaning of SEMs and Large Vacuum Systems**, ***Ronald Vane***, XEI Scientific Inc. **INVITED**

Vacuum-based processes can suffer harmful effects from the presence of adventitious hydrocarbons that result from various sources such as oils and solvents as well as work-pieces. The problem of carbon and hydrocarbon contamination in vacuum chambers of scanning electron microscopes (EM) and other ion beam instruments is well known. An effective tool at removing hydrocarbon contamination from electron microscope chambers is remote, or downstream, plasma cleaning. Electrically neutral radicals flow from the plasma source into the chamber so that carbon compounds are removed by chemical reactions.

Plasma cleaning of hydrocarbons for electron microscopes and vacuum chambers is a simple version of the more complex plasma etch and ashing technologies used in semiconductor production and other plasma processing. Its premise is straight forward: remove carbon compounds and do no damage to the instrument. Doing this requires a small plasma source that can be mounted on an instrument port. Desirable properties are 1) Use air as an oxygen source for oxygen chemical etch, 2) Avoid ion sputtering . 3) operate at low power to avoid heat and high sheath energy potential 4) Produce a narrow electron energy distribution. 5) operate over wide pressure range.

The Evactron® De-Contaminater from XEI Scientific is a hollow cathode RF plasma device that meets these criteria. First developed to operate at low vacuums produced by roughing pumps, it has been now been modified to work with high vacuum produced by turbo molecular pumps (TMP). Now Evactron cleaning can be initiated with a TMP at full speed and vacuum of < 10-7 Torr. The flow of gas through plasma raises the chamber pressure during cleaning but the TMP retains full speed. If the chamber pressure drops below 15mTorr (2 Pa) the mean free path becomes long enough that a pink flowing afterglow fills the chamber. The afterglow is the result of reduced recombination rates of radicals and metastables at the lower pressures. The flowing afterglow is a marker for the presence of the oxygen radicals that do the plasma cleaning. The cleaning volume and rates are greatly increased with flow afterglow cleaning.

The pink flowing afterglow from air plasma is caused by nitrogen metastables and contains many UV emission lines that can desorb water vapor and hydrocarbon vapors from surfaces in the chamber which speeds pump down after plasma cleaning. RGA mass spectrometry results have shown remarkable decreases of the partial pressures of all gasses in UHV chambers if flowing afterglow cleaning is done during pump down. If this effect can be used to avoid bake out of UHV systems, considerable time savings may be achieved.

3:00pm **VT-WeA3 Double Deflection and Enhanced Detection - The Use of a Novel Ion Optics for Metastable Rejection and Improved Detection in the Low ppb Range**, ***Jonathan Leslie***, MKS Instruments Spectra Products, UK **INVITED**

During electron ionisation in a Quadrupole Mass Spectrometer (QMS), metastable neutrals are produced in addition to positive ions. The ion source in current QMS Residual Gas Analysers (RGA) is coupled with "line of sight" into the mass analyser and detector. Conversion of the metastable neutral into an ion and electron can cause increased noise, especially at lower masses. The higher noise level can determine the limit of detection in the RGA. The baseline signal can vary with changes of bulk gas and/or pressure.

The use of ion optics with novel cylindrical geometries between the ion source and mass analyser, enables a focused beam of ions to be displaced onto a second parallel axis, then back to the original axis. The cylindrical geometry provides good focusing resulting in no loss of signal, combined with a simple and robust mechanical design. The tuning is robust with a single low voltage lens setting.

The theory and performance of this elegant and innovative deflection system will be discussed, highlighting applications in which it offers a competitive advantage over current RGA designs.

4:20pm **VT-WeA7 The Deployment of a Commercial RGA to the International Space Station**, ***Matthew S. Kowitt***, Stanford Research Systems*, D. Hawk,* Orbital-ATK*, D.J. Rossetti,* Conceptual Analytics*, M.S. Woronowicz*, SGT Inc. **INVITED**

The International Space Station (ISS) uses ammonia as a medium for heat transport in its Active Thermal Control System. Over time, there have been intermittent component failures and leaks in the ammonia cooling loop. One specific challenge in dealing with an ammonia leak on the exterior of the ISS is determining the exact location from which ammonia is escaping before addressing the problem.

Together, researchers and engineers from SRS and NASA's Johnson Space Center and Goddard Space Flight Center, have adapted a commercial off-the-shelf (COTS) residual gas analyzer (RGA) for repackaging and operation outside the ISS as a core component in the ISS Robotic External Leak Locator, a technology demonstration payload currently scheduled for launch during 2015. The packaging and adaptation of the COTS RGA to the Leak Locator will be discussed. The collaborative process of adapting a commercial instrument for spaceflight will also be reviewed, including the build-up of the flight units. Measurements from a full-scale thermal vacuum test will also be presented demonstrating the absolute and directional sensitivity of the RGA.

5:00pm **VT-WeA9 Temperature-stable Quartz Oscillator Applicable to Pressure Gauges, Gas Sensing, Partial Pressure Measurement, and Plasma Diagnostics**, ***Atsushi Suzuki***, AIST, Japan

A quartz friction pressure gauge (Q-gauge) is advantageous because it can measure pressures in the range of 0.01 kPa to 100 kPa and because the size of a quartz oscillator is less than 1x1 cm^2. The underlying principle of Q-gauge use in pressure measurement is that the electric impedance (*Z*) of the quartz oscillator depends on the viscosity and gas density of the measured gas. When the total absolute pressure is known, then properties related to viscosity and molecular weight can be obtained from *Z*.

This is important because it enables changes in viscosity and molecular weight of the measured gas to be detected in addition to changes in pressure. Thus, many types of methods are made possible, such as hydrogen gas sensing, hydrogen concentration measurement, partial pressure measurements of binary gas mixtures such as ozone-oxygen and silane-hydrogen, and measurements of gas decomposition efficiency and composition changes induced by plasma.

However, the disadvantage of these measurements using a quartz oscillator is that the output *Z* from the quartz oscillator is affected by temperature. This temperature dependence must be corrected in particular for uses of hydrogen sensing outdoors and in other applications in which temperature changes.

In this presentation, a novel temperature-stable quartz oscillator (TSQO) will be introduced. The output from the TSQO used in this study was the electric-impedance converted voltage, which represents *Z*. First of all, it was shown that this output depended on the total pressure from 0.01 kPa to 100 kPa, indicating that this TSQO works well as a Q-gauge device. Fluctuation of the reading output at constant temperature was 0.06% of the total output.

Temperature stability was confirmed at atmospheric pressure and for temperatures varying from 15 °C to 50 °C. With this temperature change, the change of the TSQO output was less than 0.2% of the reading output. Because the output fluctuation of a conventional quartz oscillator across the temperature range above is normally about 2.0% of the reading output, it was shown that temperature stability was attained by the TSQO. The measured degree of output fluctuation for this TSQO is acceptable for hydrogen sensing because it is smaller than the 0.2% change induced by contamination of hydrogen concentration and less than one-fourth of the fluctuation introduced by low-level explosions of hydrogen in air (4%), which is the necessary minimum detection level. Therefore, it can be concluded that this TSQO is practically useful for various measurements that involve hydrogen sensing anywhere that temperature fluctuates.

This work was supported by ISPS KAKENHI Grant Number 24560070.

5:20pm **VT-WeA10 An Ultra-high Vacuum Processing System for Constructing Small Format Photodetectors**, *D.R. Walters, R.J. Wagner,* ***John Noonan****, L. Xia, J. Xie, J. Wang, H. Zhao, M. Virgo*, Argonne National Laboratory

The Large Area Picosecond Photodetector was envisioned to be a frugal design for use in upcoming water-based Cherenkov photodetectors for the detection of neutrinos. This project's goal is to develop a glass enveloped 20 cm photodetector but to understand the issues of constructing such a detector a smaller 6 cm format was chosen to be the vehicle for parts and process development. An ultra-high vacuum system was designed and constructed for handling the sub-assemblies. This multi-chamber system is integrated so that the scrubbing, photocathode deposition, and hermetic sealing all occur within a single environment. The design of this system has process stations in adjacent chambers so that the sub-assemblies can be easily moved using magnetic linear manipulators. The vacuum performance of the system will be presented along with results on the efficiency of the photocathode, >15%, the clean-up of the scrubbing, and a brief overview of the indium vacuum seal.

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.

[1] M. M. Najafpour, E. Amini, M. Khatamian, R. Carpentier, S. I. Allakhverdiev, Journal of Photochemistry and Photobiology B: Biology (2014), 133, 124.

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 at the interfaces 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)

[3] K. E. Aretouli et al., *APL***106**, 143105 (2015)

[4] P. Tsipas et al., *Microelectron. Eng*. (2015), http://dx.doi.org/10.1016/j.mee.2015.04.113

[5] E. Xenogiannopoulou et al, *Nanoscale* **7**, 7896 (2015)

[6] F.S. Ohuchi et al., *JAP***68**, 2168 (1990)

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.

This work was supported in part by the Southwest Academy on Nanoelectronics sponsored by the Nanoelectronic Research Initiative and NIST and the Center for Low Energy Systems Technology, one of six centers supported by the STARnet phase of the Focus Center Research Program, a Semiconductor Research Corporation program sponsored by MARCO and DARPA.

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

(5) Horacio Coy Diaz, Rafik Addou, and Matthias Batzill, Nanosclae **6** (2014) 1071-1078.

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.

1. S. Förster, K. Meinel, R. Hammer, M. Trautmann, and W. Widdra, *Nature* **502**, (2013) 215.

Actinides and Rare Earths Focus Topic
Room: 230A - Session AC+AS+MI-ThM

Nuclear Power and Waste Remediation

Moderator: David Shuh, Lawrence Berkeley National Laboratory

8:00am **AC+AS+MI-ThM1 Applications of Synchrotron Methods to f-Element Research in the Nuclear Fuel Cycle**, ***Melissa Denecke***, The University of Manchester, UK **INVITED**

Celebrating 60 years of civil nuclear power generation offers an excellent opportunity to review synchrotron radiation (SR)-based techniques to characterize nuclear materials and elucidate processes relevant to the nuclear fuel cycle. The penetration capability of intense SR X-ray sources allows in situ investigations, including samples within radiological containments or specialized environments. The presentation will concentration on application of X-ray spectroscopic techniques in studies related to the nuclear fuel cycle (fuel, cladding, recycle, waste disposal).

8:40am **AC+AS+MI-ThM3 *Ab Initio* Study of Advanced Metallic Nuclear Fuels for Fast Breeder Reactors**, ***Alexander I. Landa***, Lawrence Livermore National Laboratory **INVITED**

The U-TRU-Zr and U-TRU-Mo alloys proved to be very promising fuels for TRU-burning liquid metal fast breeder reactors. The optimal composition of these alloys is determined from the condition that the fuel could remain stable in the bcc phase (γ-U) in the temperature range of stability of α-U phase. In other words, both Zr and Mo play a role of 'γ-stabilizers' helping to keep U in the metastable bcc phase upon cooling. The main advantage of U-Pu-Mo fuels over U-Pu-Zr fuels lies in much lower constituent redistribution due to the existence of a single γ-phase with bcc structure over typical fuel operation temperatures. The nucleation time for the decomposition of the metastable alloys, which controls the constituent redistribution process, is directly connected with the excess enthalpy of solution of these alloys. In the present study we perform KKR-ASA-CPA and EMTO-CPA calculations of the ground state properties of γ-U-Zr and γ-U-Mo alloys and compare their heats of formation with CALPHAD assessments. We discuss how the heat of formation in both alloys correlates with the charge transfer between the alloy components, and how the specific behavior of the density of states in the vicinity of the Fermi level promotes the stabilization of the U_2Mo compound. Our calculations prove that, due to the existence of a single γ-phase over the typical fuel operation temperatures, γ-U-Mo alloys should indeed have much lower constituent redistribution than γ-U-Zr alloys where a high degree of constituent redistribution takes place. The binodal decomposition curves for γ-based U-Zr and U-Mo solid solutions are derived from Ising-type Monte Carlo simulations incorporating effective cluster interactions obtained from the Screened Generalized Perturbation and Connolly-Williams methods. We also explore the idea of stabilization of the δ-UZr_2 compound against the α-Zr (hcp) structure due to increase of Zr d-band occupancy by the addition of U to Zr. Analogy with stabilization of the ω phase in Zr under compression is made. Though the U-Pu-Zr and U-Pu-Mo alloys can be used as nuclear fuels, a fast rector operation on a closed fuel cycle will, due to the nuclear reactions, contain significant amount of MA (Np, Am, Cm). Calculated heats of formation of bcc Pu-U, Pu-Np, Pu-Am, Pu-Cm, Pu-Zr, Pu-Mo, Np-Zr, Np-Mo, U-Am, Np-Am, Am-Zr and Am-Mo alloys are also presented and compared with CALPHAD assessments. This work was performed under the auspices of the US Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 and was funded by the Laboratory Directed Research and Development Program at LLNL under project tracking code 12-SI-008.

9:20am **AC+AS+MI-ThM5 Shedding Light on Uranium Corrosion in Nuclear Waste Packages**, ***Charilaos Paraskevoulakos***, University of Bristol, UK

Intermediate level waste (ILW) is encapsulated in grout and stored in stainless steel drums. A proportion of these have become a concern for the UK nuclear community, as significant distortion around the circumference of these drums has been observed. Distortion is ascribed to the generation of voluminous and potentially flammable corrosion products forming on uranium metal, e.g. uranium hydride. Thus potential oxygen influx caused by fracturing of canisters will threaten their suitability for waste disposal, potentially causing release of the encapsulated radioactive material or even ignition of the hydride. The association of the uranium corrosion mechanisms with the mechanical degradation of the encapsulants (stainless steel and grout), is the focus of the current project. Finite Element (FE) Modelling, accelerated uranium corrosion tests as well as diffraction and tomography using synchrotron X-Rays/gamma rays could be employed to investigate the durability of the ILW packages.

9:40am **AC+AS+MI-ThM6 The Optical Properties of Uranium Carbide Measured by Spectroscopic Ellipsometry**, ***Wigbert Siekhaus***, *A.J. Nelson, C.K. Saw*, Lawrence Livermore National Laboraatory

Uranium carbide inclusions are common in metallic uranium, and uranium carbide itself is being used or being considered as a fuel in both gas-cooled, liquid metal cooled, and supercritical water-cooled reactors. To the best of our knowledge the only study of optical properties deals with high temperature radiance. [1] Here we first characterized a uranium carbide cube (supplied by Oak Ridge National Laboratory) with sides of approximately 3 mm length by X-ray diffraction and X-ray photo-electron spectroscopy and then measured its optical properties with an ellipsometer at angles of incidence between 65 and 75 degrees, and over an energy range from 1.26 to 3.2eV. The signal strength was low over that energy range, and too low to be useful above 3.2eV. The measured Δ and Ψ were converted to the dielectric constants ε1 and ε2 shown in the table below using a general oscillator model [2].

E, eV	ε1	ε2	E, eV	ε1	ε2	E, eV	ε1	ε2
1.26	-1.96	5.07	1.95	-0.30	2.73	2.61	2.61	1.32
1.33	-1.69	4.77	2.02	-0.21	2.55	2.68	2.68	1.21
1.40	-1.47	4.45	2.10	-0.12	2.34	2.75	2.75	1.07
1.47	-1.25	4.14	2.18	-0.03	2.18	2.83	2.83	0.94
1.54	-1.06	3.87	2.25	0.04	2.02	2.91	2.91	0.85
1.61	-0.89	3.63	2.32	0.12	1.87	2.98	2.98	0.76
1.69	-0.73	3.44	2.40	0.20	1.73	3.05	3.05	0.67
1.76	-0.60	3.23	2.47	0.28	1.59	3.12	3.12	0.58
1.84	-0.48	2.95	2.54	0.35	1.43	3.20	3.20	0.51

Prepared by LLNL under Contract DE-AC52-07NA27344, LLNL-ABS-670149

[1] D. Manara, F. De Bruycker, K. Boboridis, O. Tougait, R. Eloirdi, M. Malki, High temperature radiance spectroscopy measurements of solid and liquid uranium and plutonium carbides, J Nucl Mater, 426 (2012) 126-138.

[2] R. Synowicki, J.A. Woollam CO. Inc. 645 M Street, Suite 102, Lincoln, NE 68508-2243, USA

11:00am **AC+AS+MI-ThM10 Uranium Wet Oxidation in the Presence of Hydrogen Overpressure**, ***Antonios Banos***, University of Bristol, UK

The radioactive intermediate level (IL) and high level (HL) waste have been accumulated in the UK's legacy ponds and silos for over 60 years. There is a great need for these wastes to be retrieved to follow long term storage. Uranium hydride (UH_3) has been identified as a reaction product of the corrosion process. Hydride formation occurs due to the increasing concentration of hydrogen gas, generated from the reaction of uranium, Magnox (MagnoxAl80) and other metals. The highly pyrophoric and unstable nature of UH_3 in air poses considerable environmental risks, due to potential radionuclide release. In this work we will try to simulate the corroding conditions by immersing an initially polished uranium sample in water under vacuum and introducing hydrogen gas overpressure to the system. The ternary system will be investigated in different temperatures and pressures with two main questions awaiting to be answered: 1. Is UH_3 identified? For this reason post-examination of the reacted surface will be conducted using Secondary Ion Mass Spectrometry (SIMS), Focus Ion Beam (FIB) milling. 2. If UH_3 is identified, on which part of the reaction is it produced and how this affects the overall reaction? The kinetics will be monitored using a specifically designed set-up comprised from a stainless steel pot and a pressure controller attached on one end and logged to a computer in order for the whole reaction to be recorded and the rate of corrosion through gas generation to be evaluated.

11:40am **AC+AS+MI-ThM12 Resolving the Issues of 5f Covalency and Ionicity in UO2 and UF4**, ***James Tobin***, Lawrence Livermore National Laboratory

Building upon our recent work , a concerted effort to isolate and understand covalency and ionicity in uranium compounds has been pursued. Specifically,the isoelectronic formal charge systems, uranium dioxide and uranium tetrafluoride, have been investigated with a novel mixture of both soft and hardx-ray spectroscopies. The results to be discussed will include the following: (1)the use of soft X-ray O1s/F1s X-ray absorption spectroscopy (XAS) and U4d X-ray emission spectroscopy (XES) to follow the 2p/5f bonding via the unoccupied density of states; (2) the utilization of hard X-ray U L3 extended X-ray absorptionfine structure (EXAFS) to trivially distinguish the ordering in each: and (3) the use of hard X-ray L3 resonant X-ray emission spectroscopy (RXES) to distinguish 5f occupation/covalency effects in UO2 and UF4. Collaborators include CH Booth, DK Shuh, T. Tyliszczak, G. van der Laan, D. Sokaras, T.-C. Weng, D. Nordlund, S.-W. Yu, W. Siekhaus and P.S. Bagus.

Additive Manufacturing/3D Printing Focus Topic
Room: 211A - Session AM+EM+MS+TF-ThM

Technologies Enabled by Additive Manufacturing/Future of Additive Manufacturing
Moderator: Vincent Smentkowski, General Electric Global Research Center

8:40am **AM+EM+MS+TF-ThM3 Additive Manufacturing Enabling Advanced Technologies**, ***Teresa Clement***, Raytheon Company **INVITED**

The aerospace and defense industry for the last decade has taken note and contributed to significant advances in materials and process capabilities enabled by the field of additive manufacturing (AM) to fabricate beyond state-of-the-art advanced technologies. Conventional and non-conventional industry partners continue to push the boundaries of next-generation materials and multi-materials for additive manufacturing in order to further extend product capabilities. As these material developments continue evolving, our industrial base begins to realize the many benefits of AM: reducing lifecycle costs, engineering resilience and capability surprise by rapidly reconfigurable responses to adaptive adversarial threats, and the enabling of truly agile manufacturing via AM integration with the model based enterprise (aka marrying AM to the 'digital thread'). Some specific examples of advanced technologies are discussed herein, with examples of design iteration cycle-time reduction and use of material/process controls to verify by inspection and full characterization demonstrations of improved or unprecedented material performance and multi-functionality (electrical, thermal, structural, etc) made possible by additive manufacturing.

9:20am **AM+EM+MS+TF-ThM5 4D Printing: Three Dimensional Printing with Material Composition as the Fourth Dimension**, ***Douglas C. Hofmann***, NASA Jet Propulsion Laboratory, California Institute of Technology **INVITED**

Much of the current research in additive manufacturing in the aerospace community is focused on qualifying materials for service, which is a critical requirement for using additive materials. However, additive manufacturing is a powerful tool for creating materials and applications that cannot be replicated using traditional means. In the past, this has meant 3D printing complex geometries that cannot be easily machined. In the current talk, we will discuss what we call 4D printing; 3D printing where the fourth dimension is the material composition. By using multiple materials strategically in additive manufacturing, a whole new frontier of materials science becomes possible. The science behind these alloys and their applications will be discussed.

11:00am **AM+EM+MS+TF-ThM10 The Future of Additive Manufacturing and Multifunctional Parts**, ***Phill Dickens***, University of Nottingham, UK, United Kingdom of Great Britain and Northern Ireland **INVITED**

Additive Manufacturing has many advantages for producing complex components and systems and this has already started to be exploited for parts made of a single material. There is now much interest in the possibility of building parts with multiple materials so that electrical circuits and electronic items can be included within the structure. This paper will highlight some of the research that is taking place at the University of Nottingham and some recent examples of simple products that could exploit this technology.

Some of the issues will be covered where the layer manufacturing process provides some limitations.

Applied Surface Science
Room: 212D - Session AS-ThM

Practical Surface Analysis III: Multiple-technique Problem-solving and Structure-property Correlations
Moderator: Michaeleen Pacholski, The Dow Chemical Company, Daniel Gaspar, Pacific Northwest National Laboratory

8:00am **AS-ThM1 Correlation of Substrate Surface Chemistry and Roughness to Adhesion of Pressure Sensitive Adhesives**, ***Michaeleen Pacholski***, *T. Powell, D. Keely, W.B. Griffith*, The Dow Chemical Company

This investigation focuses on the surface chemistry and roughness of substrates and the relationship to adhesion. We discuss the variability in surface chemistry and roughness of materials all nominally identified as the same material. For example, high density polyethylene (HDPE) is a common material used for bottles as well as a preferred low energy substrate for adhesion testing. However, there are several types of surface treatments used to increase adhesion. Surface roughness can also affect adhesion. We have compared corrugated cardboard surfaces and the influence of surface roughness on adhesion.

8:20am **AS-ThM2 Surface and Interface Studies of Ultra-Low Wear (ULW) PTFE/Alumina Polymer Composites**, ***Lei Zhang***, *G.S. Blackman, C.P. Junk, L. Amspacher, K.G. Lloyd, J.R. Marsh, D.J. Kasprzak*, DuPont Central Research and Development

In the past few years, polymer composites of polytetrafluoroethylene (PTFE) and alumina particles have attracted a lot of interest as a promising Ultra-Low Wear (ULW) material. It has been discovered that by adding a small amount of alumina additive (<5wt%) to PTFE, the wear rate of the PTFE is enhanced dramatically by over four orders of magnitude. Although this polymer composite system has shown its uniqueness and importance in the tribological research, the tribochemical mechanism has not been well understood.

To fully understand the chemistry that occurs during the tribology/wearing, it requires the precise design of experiments as well as applying integrated techniques to study the tribochemical process. In our studies, we investigated the tribochemical products by studying the unique chemistry of the transfer film formed at the composite and stainless steel interfaces during wearing. XPS, FTIR, and ToF-SIMS techniques have been applied to determine the chemistry of these tribochemical products as a function of number of sliding cycles. These characterization techniques have allowed us to understand the ultralow wear behavior and help to develop a conceptual framework for the ultralow wear material system.

8:40am **AS-ThM3 Investigation of Increased Glide Force of Prefilled Syringes Using Multiple Analytical Techniques**, ***Xia Dong***, *Z. Xiao, C.A.J. Kemp, G.H. Shi*, Eli Lilly and Company

Time-based glide-force changes in pre-filled syringes built into autoinjector systems can lead to negative patient experience issues and dose accuracy problems. The long term performance of prefilled syringe systems is examined during stability testing study when monoclonal antibody solutions are stored at various temperatures for given time periods. Multiple parameters including lubricant amount, lubricant distribution, and surface chemistry contribute to friction between the plunger and barrel and consequently the glide force. Therefore, it is important to understand the impact of storage conditions on lubricant characteristics and surface properties so that the desirable long term performance can be achieved.

In the current study, a monoclonal antibody solution was filled in glass syringes coated with silicone lubricant. Increased glide forces were observed from syringes stored at 25 ºC, comparing to those stored at 5 ºC. Multiple analytical techniques, including ellipsometry, ICP-OES, contact angle, XPS and TOF-SIMS were utilized to characterize lubricant and surface properties of syringe interior surfaces to understand the root cause of undesirable glide force changes.

9:00am **AS-ThM4 Degradation of Polypropylene Surgical Mesh: An XPS, FTIR, and SEM Study**, ***Bridget Rogers***, Vanderbilt University, *R.F. Dunn*, Polymer & Chemical Technologies, LLC., *S.A. Guelcher*, Vanderbilt University

Polypropylene mesh has been used to surgically treat stress urinary incontinence and has shown promising short-term results. However, serious complications have been associated with longer term implanted meshes. We hypothesize that these complications are due to oxidative degradation of the mesh brought about by reactive oxygen species that are released by adherent macrophages on the surface of the polypropylene.

Polypropylene is known to oxidize through a stable hydroperoxide (-COOH) intermediate, followed by chain scission and formation of a carbonyl (-C=O) end group. Oxidation of polypropylene leads to a reduction in molecular weight, embrittlement, cracking, and eventually fracture and fragmentation. An *in vitro* study was performed to study the oxidation of polypropylene surgical mesh in a model environment that simulates conditions the mesh would experiences in the body. Samples cut from three commercially available surgical devices produced by two manufacturers and polypropylene control samples were placed in an oxidizing medium consisting of 20% H_2O_2 and 0.1 M $CoCl_2$.

Samples were placed in the oxidizing medium and were incubated at 37 °C on a shaker for up to 6 weeks. The oxidizing medium was replaced every 3 to 4 days. Six samples were removed every week, washed in DI water, and dried. XPS and FTIR were used to analyze the samples for the presence of hydroperoxide and carbonyl species. SEM micrographs were acquired at 0, 4, and 5 weeks of oxidation.

We will present the XPS, FTIR, and SEM analytical results of the samples from this *in vitro* study. These results show that the anti-oxidants in the polypropylene mesh delay, but do not inhibit oxidation. SEM micrographs show surface pitting and flaking of samples exposed to the oxidizing medium.

9:20am **AS-ThM5 ASSD 30th Anniversary Lecture: Evolution of the Nature and Application of Surface Analysis: Challenges, Pitfalls, and Opportunities Past, Present and Future**, ***Donald Baer***, Pacific Northwest National Laboratory **INVITED**

Over the past 30 years there has been a remarkable range of advances in the ability to understand the nature of many types of important surfaces and interfaces. X-ray photoelectron spectroscopy (XPS) has become nearly essential for characterizing many types of materials, verifying the quality of synthesis methods and understanding interactions of these materials in many environments and applications. This has become possible because of major improvements in instrumentation including stability, reproducibility, increases in spatial resolution, increases in count rate, major improvements in the ability to analyze insulating samples, digital control of instruments and advances in the ability to process, model and analyze the data. For Auger electron spectroscopy (AES) similar advances have occurred, with spatial resolution being an obvious differentiator. In the area of Secondary Ion Mass Spectrometry, the major excitement has been related to the evolution of new primary and sputter beams with Bucky ball and cluster sources. Thirty years ago scanning probe methods were just beginning to appear; now they serve as critical tools for many types of studies.

In spite of the significant progress, many important materials information needs remain, providing opportunities for continued evolution of traditional surface analysis tools and the development and applications of other methods. These might be framed in the context of some “what if” questions that are not out of the range of the possible. What if we could monitor in real-time the evolution of surfaces and buried interfaces (and the actual compositional and chemical information at those interfaces) in “operational” environments? What if we could obtain quantitative compositional and chemical information at the resolution of an AFM? What if micro-technology could be used to create an XPS unit that produced quality data and operated without or with only trivial need for vacuum? What would be possible if NMR could be easily used to quantitatively characterize surfaces, interfaces or individual particles? Examples of progress along these directions will be described. All indications are that the next 30 years will be as dynamic and productive as the past 30 years, if not more so.

11:00am **AS-ThM10 Unraveling the Dynamic Nature of Mixed-Metal Oxides Nanocatalysts: An *In Situ* Multiple-Technique Approach**, ***Dario Stacchiola***, Brookhaven National Laboratory **INVITED**

Catalysts have traditionally been characterized before or after reactions and analyzed based on static representations of surface structures. It is shown here how dynamic changes on a catalyst’s chemical state and morphology can be followed during a reaction by a combination of *in situ* microscopy (AP-STM) and spectroscopy (AP-XPS and AP-IRRAS). In addition to determining the active phase of the catalyst by *in situ* methods, the presence of weakly adsorbed surface species or intermediates generated only in the presence of reactants can be determined, allowing in turn the comparison of experimental results with first principle modeling of specific reaction mechanisms. Three reactions are used to exemplify the approach: CO oxidation ($CO + 1/2O_2 \rightarrow CO_2$), water gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) and methanol synthesis ($CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$). During CO oxidation, the full conversion of Cu^0 to Cu^{+2} deactivates an initially outstanding catalyst. This can be remedied by the formation of a $TiCuO_x$ mixed-oxide that protects the presence of active partially oxidized Cu^+ cations. We also show the switch from a redox mechanism on Cu(111) to a more efficient associative mechanism pathway for the WGSR at the interface of ceria nanoparticles deposited on Cu(111) [1]. Similarly, the activation of CO_2 at the ceria/Cu(111) interface allows its facile hydrogenation to methanol [2]. Our combined studies emphasize the need of searching for optimal metal/oxide interfaces, where multifunctional sites can lead to new efficient reaction pathways.

[1] *Angew. Chem. Int. Ed.* **52**, 5101–5105 (2013)

[2] *Science*, **345**, 546-550 (2014)

11:40am **AS-ThM12 Correlation between Chemistry, Optical Properties, and Environmental Stability of DC Sputtered Rhenium Oxides**, ***Neil Murphy***, Air Force Research Laboratory, *L. Sun*, General Dynamics Information Technology, *J.G. Jones*, Air Force Research Laboratory, *J.T. Grant*, General Dynamics Information Technology

Thin films of rhenium oxide (<150 nm) are deposited using magnetron sputtering employing a rhenium cathode within an argon-oxygen atmosphere. Throughout the deposition process, the working pressure is maintained at a constant level of 1.33 Pa as the oxygen content is varied from 0% to 80% in increments of 10%. As the oxygen content is varied, the extinction coefficient, k, of the deposited layers is monitored via *in situ* ellipsometry. *In situ* ellipsometry is used to identify absorption features specific to ReO_3, including the characteristic reduction of k brought on by the optical band gap at 310 nm as well as the onset of intraband absorption above 540 nm. *In situ* ellipsometry results indicate that films deposited at oxygen levels of 50% and 60% have resepective k_{450} values of 0.6 and 0.25, characteristic of ReO_3. Chemical analysis via x-ray photoelectron spectroscopy confirmed that films individually deposited at oxygen levels of 50% and 60% are mixed-valent, consisting largely of ReO_3 (Re^{6+}), with contributions from ReO_2 (Re^{4+}) and Re_2O_7 (Re^{7+}). Note that films deposited at 50% oxygen content also contained up to 15% Re_2O_3 (Re^{3+}). Further monitoring of the films’ valence states, after an environmental exposure time of 30 days, indicates a correlation between structural instability and the presence of both Re_2O_3 and Re_2O_7. Analyses via XPS and *ex situ* spectroscopic ellipsometry indicate that films deposited within an atmosphere of 60%oxygen do not contain Re^{3+} and demonstrate stable surface chemistry and optical behavior throughout the 30 day period, while those deposited at 50% oxygen experience significant degradation. Increasing the stability of mixed-valent Re-O films could give rise to more widespread use of rhenium in optics and catalysis, especially in applications where mild moisture exposure is unavoidable.

12:00pm **AS-ThM13 Multi-Technique Surface Analysis of Geological Samples, Including sub-10 Micron Spectroscopic XPS Imaging**, ***Paul Mack***, Thermo Fisher Scientific, UK

A single geological sample may have multiple phases, each with different chemical bonding environments. Geologists will typically have access to SEM-EDS, giving them elemental information from the different grains (from bulk depths). When it comes to chemical information, however, XPS provides a unique ability to easily acquire data from these small grains. It offers quantitative chemical bonding data with a probe size small enough to acquire data from individual phases.

In this work, rock cross-sections were analysed with XPS to quantify the elements in different phases and to identify and quantify the oxidation states of elements in these regions. The analysis can be divided into four main sections: 1) Finding the features of interest, 2) Aligning the X-ray spot on the features, 3) Acquiring the XPS data and 4) Processing the XPS data to answer the key questions about chemical bonding states.

Any XPS tool used for this analysis needs to have a high quality optical system, enabling to geologist to rapidly find the features of interest, with a live optical feedback system. The grains were typically 10s of microns in size, so a small X-ray analysis area is required. This small area analysis was achieved in two different ways: shrinking the

X-ray spot to match the feature size or collecting spectroscopic parallel imaging data. In the latter case, every pixel in the image has full XPS data allowing the analyst to perform sub-10mm area analysis directly from the X-ray image.

Techniques complementary to XPS can also help provide a more complete characterization of geological samples. SEM/Auger can offer analysis with a much smaller probe size than XPS, but it is necessary to charge compensate during the experiment. Charge compensation methodology will be discussed in this work.

Spectroscopic Ellipsometry Focus Topic
Room: 112 - Session EL+EM+EN-ThM

Spectroscopic Ellipsometry: Novel Applications and Theoretical Approaches

Moderator: Tino Hofmann, University of Nebraska - Lincoln, Vimal Kamineni, Globalfoundries, Ny, Usa

8:00am **EL+EM+EN-ThM1 Multi-Spectral Polarimetric Imaging and Biomedical Applications**, ***Bernard Drevillon***, *A. Pierangelo*, LPICM-CNRS, Ecole Polytechnique, France **INVITED**

In the last years Polarimetric Imaging has received considerable attention in the literature thanks to its tremendous potential for the assessment of biological tissues in biomedical diagnostics. Light Polarization allows obtaining morphological information on tissues microscopic structure, potentially improving the diagnosis and treatment of several pathologies. Moreover, polarimetric imaging can be implemented using conventional light sources, like LED or halogen lamps, making it a cheap alternative to current standards. For several years the PICM Laboratory has designed and built innovative polarimetric imagers for biomedical applications. In particular, the development of the *eigenvalue calibration method* [1], led to the design of several polarimeters for macroscopic and microscopic analysis (in real and Fourier space) of *ex vivo* samples and for *in vivo* diagnoses. The development of such new instruments ranged from the simple measurement of polarization degree to the complete Mueller polarimetry. Several studies were devoted to the early detection and staging of uterine cervix cancer and to show that polarimetric imaging is effective for the visualisation and first grading of cervical dysplastic regions for patients with anomalous Pap smear [2]. Mueller matrix imaging polarimetry also provides enhanced contrast to differentiate types of cancer of colon and their stage of progress and penetration, which is currently detectable only by histological examination [3]. Moreover, this technique may also be useful to quickly verify the presence of residual cancer in the rectum after treatment with radiochemotherapy [4]. Finally, as a complementary development to experimental techniques, the set-up of Monte-Carlo detailed modelling of polarized light scattering in tissues has been carried out in the last few years and provides fundamental insight on the origin of observed polarimetric contrasts [5]. In conclusion the synergy of new experimental techniques based on polarimetry with the biomedical analysis and theoretical computer models, led to significant advances in the field of biological tissues characterization and diagnosis of related pathologies.

[1] E. Compain et al., Appl. Opt. 38, 3490-3502 (1999).

[2] A. Pierangelo et al., Opt. Express, 21, 14120 -14130 (2013).

[3] A. Pierangelo et al., Opt. Express 19, 1582 (2011).

[4] A. Pierangelo et al., J. Biomed. Opt., 18 (04), 046014 (2013).

[5] M.R. Antonelli et al., Opt. Express 18, 10201 (2010).

8:40am **EL+EM+EN-ThM3 Anisotropic Optical Properties of Rhombohedral and Tetragonal BiFeO$_3$ Phases**, ***Daniel Schmidt***, National University of Singapore, *L. You,* Nanyang Technological University, Singapore, *X. Chi,* National University of Singapore, *J. Wang,* Nanyang Technological University, Singapore, *A. Rusydi*, National University of Singapore

Single crystalline bismuth ferrite (BiFeO$_3$) is a multiferroic perovskite structure and exhibits magnetic as well as strong ferroelectric behaviour at room-temperature. Since about a decade BiFeO$_3$ is of strong research interest due to its potential applicability in ferroelectric memory devices and spintronics, for example [1].

While the lattice system of bulk BiFeO$_3$ is rhombohedral, the crystal structure of thin films can be engineered by introducing epitaxial strain. Depending on the choice of single crystalline substrate materials the thin film BiFeO$_3$ crystal structure and associated physical properties can be modified.

Here, we present the anisotropic optical properties of high-quality multiferroic BiFeO$_3$ thin films determined with Mueller matrix ellipsometry at room-temperature within the spectral range of 0.6 and 6.5 eV. The full dielectric function tensors of tetragonal-like and rhombohedral-like BiFeO$_3$ phases epitaxially grown on LaAlO$_3$ and SrTiO$_3$ single crystal substrates, respectively, are discussed. Significant birefringence and dichroism are observed as well as strain-induced differences in critical point energies between both phases.

The importance of careful optical analysis of anisotropic Mueller matrix data will be discussed, which allows for characterization of subtle sub-band gap crystal field transitions and reveals indications of an indirect band gap. Such transitions have been observed before by means of other techniques but not by ellipsometry. Additionally, the analysis of Mueller matrix data revealed that an unintentional substrate miscut can introduce an overall polarization tilt of the ferroelectric thin films. This tilt was confirmed by extensive in- and out-of-plane piezoelectric force microscopy studies.

An accurate determination of the dielectric function tensor is of high importance to verify or, if necessary, improve and correct ab-inito calculations, which are crucial for understanding the driving physical principles in such complex materials. A comparison of the experimental results with state-of-the art first-principle calculations will be presented.

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9:00am **EL+EM+EN-ThM4 Temperature Dependent Structural and Optical Properties of SnO$_2$ Thin Film**, ***Junbo Gong***, *R.C. Dai, Z.P. Wang, Z.M. Zhang, Z.J. Ding*, University of Science and Technology of China

SnO$_2$, which is an n-type semiconducting material with a wide band gap 4 eV, is an interesting material due to its high electrical conductivity and optical transparency. SnO$_2$ film is attractive for many applications such as optoelectronic devices, gas sensors, thin film transistors, transparent electrodes, anti-reflecting coating, and as catalyst support.

In this work, the ellipsometric parameters of SnO$_2$ films on quartz glass are measured by spectra ellipsometer(J. A. Woollam M-2000U) in the wavelength range of 300 to 1000 nm at different temperature from room temperature to 600 ^{o}C. By using a semitransparent model, the precise thickness and optical constants of SnO$_2$ thin film depending on the temperature were obtained and the evolution process was studied. The film thickness significantly decreased with increased temperature from 100 ^{o}C to 300 ^{o}C and the absorption edge has an obvious blue shift which means an increased band gap. The result reveals that this process is not reversible. Combined with XRD measurement, we identified that the change of thickness and optical properties of SnO$_2$ film was due to a phase transition from rutile structure to columbite structure.

9:20am **EL+EM+EN-ThM5 Determining Curvature Radius of a Curved Surface by use of Mueller Matrix Ellipsometry**, ***Weiqi Li***, *H. Jiang, C.W. Zhang, X.G. Chen, S.Y. Liu*, Huazhong University of Science and Technology, China

Determining curvature radius of a curved surface by use of Mueller matrix ellipsometry

Weiqi Li, Hao Jiang, Chuanwei Zhang, Xiuguo Chen, and Shiyuan Liu*

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Ellipsometry is a powerful metrology tool for the characterization of surfaces and thin films. Generally, the basic principle of conventional ellipsometry is based on the assumption that the studied film or structure is on a planar surface [1], in another word, the conventional ellipsometry works the best for a flat surface. When the studied surface is tilted or curved, the measurement accuracy of the conventional ellipsometry will be significantly degraded, or even be incorrect. It is thus important to develop a method to deal with the cases when the surface for characterization is tilted or curved. Comparing with the conventional ellipsometry, the Mueller matrix ellipsometry (MME) can provide all 16 elements of a 4 by 4 Mueller matrix, and consequently can acquire much more useful information about the curved surface and thereby shows great potential in the curved surface metrology.

In this work, we propose an optical model that is able to process curved surface based on our in-house developed dual rotating-compensator MME [2] to characterize the surface layer of a single crystal silicon sphere crown with a radius of about 51 mm for demonstration. Focus probe accessory is used in the MME to achieve sufficient small spot on the curved surface so that the detected area on the spherical surface can be approximately regarded as a tilted one. We found that some of the measured off-diagonal Mueller matrix elements are very sensitive to the offset between the actual detected spot and the surface vertex, which is proportional to the deviation angle α of the surface normal across the surface vertex. An optical model of the spherical layer is proposed by considering the curved surface of the silicon sphere crown and the offset. With the proposed model, the deviation angle α as well as the surface layer thickness can be extracted from the measured Mueller matrix spectrum, and then the curvature radius of the sphere crown can be achieved. Experiments are performed on the silicon sphere crown show that not only the accuracy of measurement can be improved but also the curvature radius of the sphere crown is capable to be measured using the proposed optical model.

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9:40am **EL+EM+EN-ThM6 Cavity-Enhanced Optical Hall Effect in AlInN/GaN-based HEMT Structures Detected at Terahertz Frequencies**, ***Sean Knight***, University of Nebraska-Lincoln, *S. Schöche,* J.A. Woollam Co. Inc., *V. Darakchieva, P. Kühne,* Linköping University, Sweden, *J.-F. Carlin, N. Grandjean,* Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, *C.M. Herzinger,* J.A. Woollam Co. Inc., *M. Schubert, T. Hofmann*, University of Nebraska-Lincoln

The terahertz optical Hall effect (THz-OHE) has been established as a non-contact and therefore valuable tool for the investigation of free charge carrier properties in semiconductor heterostructures [1-4]. In this work, we demonstrate that the THz-OHE signal for samples grown on THz transparent substrates can be controlled and enhanced by a tunable, externally coupled Fabry-Pérot cavity mode [5]. An AlInN/GaN-based high electron mobility transistor structure (HEMT) grown on a sapphire substrate is investigated as an example, while the cavity enhancement phenomenon discussed here is generally applicable to situations when a layered sample is deposited onto a THz transparent substrate. We show that in the vicinity of an externally coupled-cavity mode, a strong enhancement of the OHE signatures of up to one order of magnitude can be achieved by optimizing the cavity geometry, which is very useful for small magnetic field strengths. This signal enhancement allows the determination of free charge carrier effective mass, mobility, and density parameters using OHE measurements in low magnetic fields. Previously, high-field electromagnets needed to be employed for THz-OHE measurement for the determination of free charge carrier parameters in semiconductor heterostructures. Tuning the external cavity allows an enhancement of the THz-OHE signatures by as much as one order of magnitude. We propose to employ this enhancement effect to reliably and accurately determine free charge carrier properties in semiconductor structures at small magnetic fields dispensing with the need for expensive high magnetic fields. Cavity-enhanced THz-OHE may therefore enable the wide spread contactless measurement of free charge carrier properties at THz frequencies and which is indispensable for the development of the next generation of group-III nitride-based high frequency devices.

11:00am **EL+EM+EN-ThM10 Biosensor based on Imaging Ellipsometry and its Biomedical Applications**, *Y. Niu,* ***Gang Jin***, Institute of Mechanics, Chinese Academy of Sciences, China **INVITED**

The concept of biosensor based on imaging ellipsometry (BIE) was proposed in 1995 [1, 2]. With the development in recent 20 years, it has been formed an automatic analysis technique for detecting biomolecule detection interaction with merits of rapid, label-free, quantitative, high throughput and real-time. Its principle, methodology, biosensor system and biomedical applications are reviewed in this report.

A BIE system can be divided into four parts: the microfluidic array reactor, the imaging ellipsometer, the control system, and the biosensor database. The microfluidic array reactor serves to fabricate the protein microarray and accommodate biomolecular interactions. Using the microfluidic array reactor, various ligands are immobilized to different cells to form a sensing array, and each sensing surface can be prepared homogeneously under the flow condition. The imaging ellipsometer acts as a reader for data acquisition from the microarray. Since imaging ellipsometry is sensitive to slight variations of optical thickness, it can be used to visualize ultra-thin films and the change of molecular mass surface concentration. The control system combines the reactor with the imaging ellipsometer and functions to control the hardware's mechanical motion and obtain results in images, while the biosensor database is to aid BIE users in determining optimized experimental conditions and comparing previous test data.

The sensitivity and flexibility of the biosensor is very important for practical purpose, especially in biomedical fields. The sensitivity depends not only upon the resolution of imaging ellipsometry but also upon the bio-system of ligand-receptor on the microarray that is the bioactivity and its act related to the ligand screen, ligand immobilization, unspecific blocking and interaction conditions, etc. The flexibility mainly depends on the mechanical, electrical, informatics and biological control. So far, a serviceable engineering system of the biosensor and some bio-systems is installed available for more applications, especially for high throughput protein analysis, such as antibody screening [3], disease markers serological detection [4] and joint detection of tumor markers [5] as well as virus infection identification [6-7].

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11:40am **EL+EM+EN-ThM12 Screening Breast Cancer by Joint Detection of Tumor Marker Carbohydrate Antigen 15-3 and Carbohydrate Antigen 242 with Biosensor Based on Imaging Ellipsometry**, ***Yu Niu****, G. Jin*, Institute of Mechanics, Chinese Academy of Sciences, China

Breast cancer which develops from breast tissue is the leading type of cancer in women worldwide, accounting for more than 25% of all carcinogenesis [1]. Compared with other common cancers, the survival rate of breast cancer is remarkably positive and optimistic that between 80% and 90% of those in developed country could be alive for at least 5 years. Therefore, screening high risk population and further concluding a clinical diagnosis in the early stage act as a pivotal factor to cure breast cancer, because it can provide overwhelming contribution to carry out essential therapy in time. Carbohydrate Antigen 15-3 (CA 15-3) and Carbohydrate Antigen 242 (CA 242) are widely-used tumor markers for breast cancer in clinic and their concentrations in serum vary sensitively with breast cancer genesis. The biosensor based on imaging ellipsometry (BIE) for visualization of biomolecular interactions was reported in 1995 [2] and now it is composed of a 48 protein unit array and imaging ellipsometry reader with a field of view (20 x 30 mm) and good resolution for protein adsorption layer on a silicon substrate (lateral and vertical is 1 μm and 0.1 nm, respectively) [3]. In this investigation, joint detection of these two tumor markers simultaneously has been performed with BIE as a trial for screening breast cancer for clinical purpose.

To realize the joint detection, a series of design and optimization has been performed, including the ellipsometric setting, ligand immobilization strategy, ligand surface density, as well as the blocking and rinsing procedures. The test concentration range calibration and the detection limit for quantitative detection have been established by standard samples, which meet the standards of clinical test. By diluting sera to the detection range fitting to the calibration curves, joint quantitative detection of CA 15-3 and CA 242 can be achieved simultaneously.

149 serum samples composed of both the healthy and patients have been performed with BIE. Compared with the results obtained by standard approaches in clinic, the correlation analysis indicates the BIE are highly consistent with clinical methods. In order to estimate the BIE performance for tumor markers detection, ROC curve analysis has been introduced. Its result suggests that the single marker detection by BIE presents good capability to distinguish the normal from patients and the joint detection of CA 15-3 and CA 242 plays a positive role in the improvement of the diagnosis specificity and accuracy.

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12:00pm **EL+EM+EN-ThM13 Decomposition of Angle Resolved Spectroscopic Mueller Matrices from Scarabaeidae Beetles**, ***Roger Magnusson***, Linköping University, Sweden, *R. Ossikovski, E. Garcia-Caurel,* LPICM-CNRS, Ecole Polytechnique, France, *K. Järrendahl, H. Arwin*, Linköping University, Sweden

We use angle-dependent Mueller-matrix spectroscopic ellipsometry (MMSE) to determine Mueller matrices of Scarabaeidae beetles which show fascinating reflection properties due to structural phenomena in the exocuticle which are often depolarizing. It has been shown by Cloude [1] that a depolarizing matrix can be decomposed into a sum of up to four non-depolarizing matrices according to $\mathbf{M}= a\mathbf{M}_1+b\mathbf{M}_2+c\mathbf{M}_3+d\mathbf{M}_4$, where a, b, c and d are eigenvalues of the covariance matrix of $\mathbf{M}$. Using the same eigenvalues the matrices $\mathbf{M}_i$ can be calculated. This method provides the full solution to the decomposition with both the non-depolarizing matrices and the weight of each of them in the sum.

An alternative to Cloude decomposition is *regression decomposition*. Here any Mueller matrix can be decomposed into a set of matrices $\mathbf{M}_i$ which are specified beforehand. Whereas in Cloude decomposition the only constraint on the matrices is that they are physically realizable non-depolarizing Mueller matrices, we can now limit the constraint and only use Mueller matrices representing pure optical devices having direct physical meaning, such as polarizers, retarders, etc. This leaves a, b, c, d as fit parameters to minimize the Frobenius norm $\mathbf{M}^{exp}$ -$\mathbf{M}^{reg}$ where $\mathbf{M}^{exp}$ is the experimentally determined Mueller matrix to be decomposed and $\mathbf{M}^{reg}$ is the sum of all $\mathbf{M}_i$. Depending on $\mathbf{M}^{exp}$ an appropriate choice of $\mathbf{M}^{reg}$ matrices has to be made and different values of a, b, c and d are obtained through regression analysis.

We have previously shown that regression decomposition can be used to show that the Mueller matrix of *Cetonia aurata* can be decomposed into a sum of a circular polarizer and a mirror [2]. Here we expand the analysis to include angle-resolved spectral Mueller matrices, and also include more species of Scarabaeidae beetles.

One effect of the decomposition is that when depolarization is caused by an inhomogeneous sample with regions of different optical properties the Mueller matrices of the different regions can be retrieved under certain conditions. Regression decomposition also has potential to be a classification tool for biological samples where a set of standard matrices are used in the decomposition and the parameters a, b, c, d are used to quantify the polarizing properties of the sample.

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Electronic Materials and Processing
Room: 210E - Session EM+MS-ThM

III-N Nitrides for Optoelectronic Applications

Moderator: Rachael Myers-Ward, U.S. Naval Research Laboratory, Aubrey Hanbicki, U.S. Naval Research Laboratory

8:00am **EM+MS-ThM1 Hollow Cathode Plasma-Assisted Atomic Layer Deposition of Wurtzite InN and $In_xGa_{1-x}N$ Thin Films with Low Impurity Content**, ***Ali Haider****, S. Kizir, C. Ozgit-Akgun, E. Goldenberg, M. Alevli, A. Kemal Okyay, N. Biyikli*, Bilkent University, Turkey

Among the III-nitride compound semiconductor family, InN is known with its unique properties which are crucial for both electronic and optoelectronic applications such as narrow band gap, small effective mass, and high electron mobility. Since InN and its alloys are currently the backbone of LED industry for bandgap tuning and are mostly grown using high-temperature epitaxy, experimental efforts on enabling low-temperature growth are critical to widen its perspective for applications like flexible (opto)electronics. In addition, a growth method in which indium composition can be precisely controlled for $In_xGa_{1-x}N$ alloys is highly imperative for band gap engineering.

In this work, we summarize our recent progress on the development of crystalline InN and $In_xGa_{1-x}N$ thin films with low impurity content at a substrate temperature as low as 200 °C by hollow cathode plasma-assisted ALD (HCPA-ALD). Deposition of polycrystalline wurtzite InN thin films was achieved using trimethylindium ($InMe_3$) and N_2 plasma sources. Process parameters including $InMe_3$ pulse time, N_2 flow rate and duration, purge time, deposition temperature, and plasma power were investigated. Detailed structural and optical characterizations of InN and $In_xGa_{1-x}N$ were performed. N_2 plasma exposure time had a profound effect on the impurity content of the InN films. After saturating the surface of substrate with $InMe_3$ molecules, the ligands of $InMe_3$ were removed completely only after sufficient exposure dose of N_2 plasma. Insufficient exposure times of N_2 plasma resulted in InN films with higher carbon impurity contents as determined from XPS measurements, which were arising from methyl ligands of $InMe_3$. After optimizing the precursor dosages,XPS survey scan obtained from the bulk part of the InN film showed that *h*-InN films were carbon and oxygen free. On the other hand, indium composition in different $In_xGa_{1-x}N$ thin films was determined by energy-dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, and X- ray diffraction. GIXRD measurements revealed the hexagonal wurtzite crystalline structure of the grown InN and $In_xGa_{1-x}N$ thin films. Refractive index of the InN film at 750 nm was estimated to be 2.67 while refractive indices of $In_xGa_{1-x}N$ thin films increased from 2.28 to 2.42 at wavelength of 650 nm with increase in indium composition. Optical band edge studies of the $In_xGa_{1-x}N$ films confirmed the successful tunability of the optical band-edge with alloy composition. Our results show that HCPA-ALD is an alternative technique to grow crystalline InN and $In_xGa_{1-x}N$ films at low substrate temperatures.

8:20am **EM+MS-ThM2 Infrared Nanoscopy of Indium-rich InGaN Epilayers**, ***Yohannes Abate***, *D. Seidlitz, N. Dietz*, Georgia State University, *I. Ferguson*, Missouri University of Science and Technology

The unique optical and electrical properties of ternary $In_{1-x}Ga_xN$ epilayers and heterostructures therewith makes this material system attractive for various optoelectronic device applications, including but not limited to high-speed electronics, frequency agile photovoltaic solar cells, or light emitting devices. However, the presently utilized growth methods enable the indium incorporation in $In_{1-x}Ga_xN$ heterostructures to a narrow composition range, before phase instabilities are encountered. As a potential pathway to extend the stable composition range and the control of point defects in the alloys, we explored in recent years the reactor pressure dependency under superatmospheric MOCVD - also denoted high-pressure chemical vapor deposition (HPCVD) - conditions. In this contribution we will report and discuss on the growth of indium-rich ternary $In_{1-x}Ga_xN$ epilayers and the influence of the pulse separations on the phase purity and stability of indium-rich $In_{1-x}Ga_xN$ epilayer and resulting structural and optical properties. The InGaN epilayers have been characterized by x-ray diffraction, Raman spectroscopy, atomic force microscopy, and by several optical techniques such as infrared (IR) reflectance and optical absorption spectroscopy. The free carrier concentrations have been estimated by analyzing the IR-reflectance spectra and by Raman A1(LO) mode line shape analysis.

8:40am **EM+MS-ThM3 Surface Treatment and Characterization of InN (0001)**, *S.P. Park, T. Kaufman-Osborn, K. Sardashti,* University of California San Diego, *S.M. Islam, D. Jena,* University of Notre Dame, ***Hyunwoong Kim***, *A.C. Kummel*, University of California San Diego

Indium nitride (InN) is a promising material due to the its band offset to GaN. However, employing InN in practical devices is still challenging because it has an electron accumulation at the surface which is hypothesized to be due to an In-In double layer at the surface. For practical InN devices, it is critical to remove this In-In double layer and form a non-metallic surface. This work describes the transformation of the atomic order, elemental composition, and electric structure of InN (0001) surface during the removal of the metallic layer and its replacement with gate oxide using scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy (XPS), and scanning tunneling spectroscopy (STS). Three cleaning methods were studied. (1) Ex -situ wet cleaning was performed by using HCl, NH OH, and (NH) S solution to remove native oxide. STM showed the surface is smooth and uniform and STS showed n-type conductivity with a band gap of 0.7 eV consistent with strong intrinsic accumulation of electrons on the surface. (2) In-situ atomic hydrogen cleaning on wet cleaned InN surface was performed. However, due to the preferential nitrogen depletion in atomic hydrogen cleaning, the ratio of indium to nitrogen was increased. STM images showed rows of indium dimers, and STS showed that there was a metallic zero band gap surface, consistent with an In-In double layer surface termination. (3) As an alternative method to eliminate the accumulation of electron at InN surface, an O passivation was performed on wet cleaned InN. The O exposed surface was atomically flat and uniform. STM line traces showed islands were formed with step height of 3.5 angstrom consistent with formation of an O-In-O layer. The band gap of the O passivated InN surface was 0.8 eV and the Fermi level was midgap consistent with absence of In-In double layer.ALD nucleation was studied using TMA pre-dosing and an additional 10 cycles of TMA and H_2O doses on an O_2 passivated InN substrate. After the 10 cycles of ALD, the ratio of Al to O ratio was 2:3 consistent with the stoichiometric ratio of Al_2O_3, The ALD process broadened the band gap from 0.8 eV to 1 eV due to the formation of Al-O-Al bonding, In sum, an unpinned non-metallic surface without the formation of In-In layer was achieved on InN using an oxidant and cyclic dose of TMA and water.

9:00am **EM+MS-ThM4 State-Of-The-Art High Efficiency Thermoelectric Material: III-Nitrides as a Wide Bandgap Semiconductor**, *B. Kucukgok, N. Lu,* University of North Carolina at Charlotte, ***Nikolaus Dietz***, Georgia State University, *I. Ferguson*, Missouri University of Science and Technology

Thermoelectric (TE) devices have gained widespread interest as a renewable energy source in the field of energy conservation and emission reduction due to their direct conversion of heat into electricity by Seebeck effect of TE materials. Additionally, TE devices have been used in wide variety of applications, due to their reliability, stability, and low-cost, such as automotive industry, spacecraft radioisotope power supply, and photovoltaic solar cells. Since TE device performance is directly related to material efficiency, material selection becomes essential. Recently, the interest of potential applications of III-nitride semiconductors in the TE field has been initiated due to their distinguished features including high-temperature operation, high mechanical strength, and large-band gap range and their promising TE figures of merit (*ZT*), mostly for materials based on AlGaN and InGaN alloys. Here, we demonstrate the room temperature thermoelectric properties of III-nitrides such as GaN and its alloys, grown by metalorganic chemical vapor deposition (MOCVD). The structural, optical, electrical, and thermal properties of the samples were examined by X-ray diffraction, photoluminescence, van der Pauw hall-effect, and thermal gradient methods, respectively. The objectives of this paper are to understand the role of defects, carrier density *n*, and composition *x* on the TE properties of III-nitrides.

9:20am **EM+MS-ThM5 Nanofabrication of Advanced Nanophotonic Structures by Nanoimprinting**, ***Stefano Cabrini***, Lawrence Berkeley National Laboratory (LBNL) **INVITED**

To exploit the potentialities of Nanophotonics, it is important to control the properties of the material at the nanometer scale, obtaining a good agreement between the experiments and the theory. Nanofabrication can open the way for new concept of devices. In this presentation we will present the fabrication and characterization of simple photonic crystals directly pattern by nanoimprinting using a special functional resist with high refractive index.

11:00am **EM+MS-ThM10 Advanced III-Nitride Device for RF Switch Applications: A Record 2THz Fco Super-Lattice Castellated Field Effect Transistor (SLCFET) for Low Loss RF Switching**, ***Shalini Gupta***, *R. Howell, E. Stewart, J. Parke, B. Nechay, M. King, H. Cramer, J. Hartman, R. Freitag, M. Snook, I. Wathuthanthri, G. Henry, K. Renaldo*, Northrop Grumman ES **INVITED**

Northrop Grumman Electronic Systems (NGES) reports on the development of a novel field effect transistor structure, based on a super-lattice epitaxial layer combined with a three dimensional castellated gate structure to achieve a 3x improvement in RF switch figure of merit compared to current state of the art transistor technologies. RF switch components are vital for the successful implementation of a variety of system architectures, spanning applications from phased array radars to the wireless components of mobile phones and consumer electronics.

NGES used MOCVD growth techniques to grow a GaN/AlGaN based super-lattice on a 100 mm diameter semi-insulating SiC substrate which is used as the SLCFET conductive channel. This super-lattice creates multiple 2DEGs producing parallel current channels between the source and drain of the device resulting in currents several times higher than conventional FETs and a record low GaN epi sheet resistance of 60 ohm/sq. The low epi sheet resistance in turn reduces the on resistance of the FET which results in a low insertion loss RF switch. Although super-lattice structures have been employed to make optoelectronic semiconductor devices, their use in FETs have been limited due to difficulty in pinching-off the stacked paralleled current channels. This is because the top channels screen the bottom channels from the electric field of the gate thereby increasing the voltage needed to pinch off the channel and turn off the device to a value beyond the breakdown field of the semiconductor. The SLCFET overcomes this challenge by employing a side-pinching gate. This is realized by etching features in the semiconductor prior to a 0.25 um gate deposition which allows the gate metal to surround the channels on the top and sides. This feature resembles the crenellations of a castle and hence is called a castellated gate.

Electrical measurements of the SLCFET transistor reveal a high I_{MAX} of 2.7 A/mm and a pinch off voltage of -8V. The SLCFET has a low on resistance (R_{ON}) of 0.4 Ohm-mm and an off capacitance (C_{OFF}) of 0.2 pF/mm, resulting in an RF switch figure of merit ($Fco = 1/2\pi R_{ON}C_{OFF}$) of 2 THz, 3x higher than the current state of the art FET based RF switches. SLCFET MMICs have been designed and tested including Single Pole Double Throw (SPDT) switches, tunable filters, and true time delay units. State of the art electrical results have been obtained, such as a series-shunt broadband (1-18 GHz) SLCFET SPDT with a measured insertion loss of 0.25 dB at 10 GHz, with -35 dB of isolation and -23 dB of return loss. These state-of-the-art results demonstrate that SLCFET is an enabling technology for next generation RF systems.

11:40am **EM+MS-ThM12 Developing Periodically Oriented Gallium Nitride for Frequency Conversion**, ***Jennifer Hite**, R. Goswami, J.A. Freitas, M.A. Mastro, I. Vurgaftman, J.R. Meyer,* U.S. Naval Research Laboratory, *C.G. Brown,* University Research Foundation, *F.J. Kub, S.R. Bowman, C.R. Eddy, Jr.*, U.S. Naval Research Laboratory

Gallium nitride is a semiconductor widely used in both optical and electronic devices. The polarity of GaN (+/- c-direction) influences many properties of the resultant material, including chemical reactivity and electric field in these 'spontaneously polarized' materials. By engineering inversion layers, we have demonstrated control of GaN polarity on both polar faces of GaN. By employing a selective growth method to deposit the IL, the lateral polarity of the GaN can be alternated, thus enabling structures referred to as periodically oriented (PO) GaN.

On N-polar substrates, we demonstrated that optimization of the MOCVD growth rates resulted in sharp, vertical interfaces and smooth surfaces. This work has moved the technology substantially closer to practical non-linear optic emitters by using HVPE to extend the PO GaN templates on N-polar substrates to total thicknesses of up to 500 mm, while faithfully maintaining the pattern of alternating polarity. Additionally, cross-sectional cathode-luminescence (CL) imaging of such an extension shows that the large initial dislocation densities occurring in the original inversion layers greatly decreased after about 25 µm of regrowth.

For growth on Ga-polar substrates, we have demonstrated that inversion layers can be created using atomic layer deposition (ALD) of Al_2O_3. This new capability is especially relevant because Ga-polar films are more prominent in devices, as they result in lower impurities, higher quality and smoother films. In this case, GaN grown over the inversion layer is N-polar. This inversion layer was used to form laterally-patterned stripes of alternating Ga- and N-polar films. We find that annealing the ALD films crystallizes the Al_2O_3, thereby allowing N-polar GaN to be grown over the new sapphire-like surface. Transmission electron microscopy shows that the inversion layer in a PO GaN structure is crystalline, a-plane oriented, and a-phase. TEM characterization further indicates that the GaN layers, both above and below the Al_2O_3 inversion layer, are c-oriented without any rotation between them. The optimization of this process has enhanced the surface smoothness. The latest results in demonstrating secondary harmonic generation will be presented.

These methods of GaN polarity inversion offer the promise of engineered materials with custom lateral and vertical polarity variations for applications in novel electronic and optoelectronic devices, a subset of which are expected to be suitable for non-linear optics.

12:00pm **EM+MS-ThM13 Electronic and Optical Device Applications based on III-Nitride Films Grown by Plasma-Assisted ALD**, *B. Tekcan, **Sami Bolat**, C. Ozgit-Akgun, N. Biyikli, A.K. Okyay*, Bilkent University, Turkey

For many electronic and optical applications, III-nitride materials are much sought after due to their direct and high optical band-gap, high electron saturation velocity and band-gap tunability [1]. These important features enable many possible device applications, which are generally used in high power and high frequency applications [2]. However, these films are generally grown using high temperature and high vacuum processes namely, MOCVD [3], MBE [4] which limit substrate selection along with CMOS compatibility. In our work, we offer an alternative way of growth to fabricate thin film transistors (TFTs) and UV metal-semiconductor-metal (MSM) photodetectors. Hollow cathode plasma assisted Atomic Layer Deposition (HC-PA-ALD) technique make low temperature device applications possible. We have grown GaN and InGaN films and analyzed TFT and photodetector properties in detail. Electrical and optical characteristics of these devices are inspected.

The results can pave the way for ALD to be used for III-Nitride based electronic and optical devices. Thin film transistor exhibit $2x10^3$ ON/OFF ratio with threshold voltage of 11.8 V. Metal-semiconductor-metal (MSM) photodetectors, on the other hand, showed 20 pA under -20 V voltage bias with a UV responsivity of 680 m A/W under 290 nm incident light with only a 20 nm thick film. Effect of annealing on the device performance is also studied. TFTs ON/OFF ratio increased to $2x10^4$ with a lower threshold voltage and contact resistance decreased 4000 times when annealed at 800 °C for 30 seconds. Moreover, MSM devices performance also enhanced after annealing 600 °C. The photoresponsivity as high as 950 m A/W at 290 nm incident light is recorded. The dark current reduced significantly, a current value of 50 fA is recorded under -20 V voltage bias.

Along with GaN devices, InGaN based photodetectors are fabricated and characterized. MSM devices based on InGaN devices showed responsivity and dark current levels controlled by In concentration. The resistivity of the films decreased with concentration of In in the semiconductor. Changing the In concentration, bandgap tunability is possible.

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Electronic Materials and Processing
Room: 211C - Session EM-ThM

Interconnects II
Moderator: Andy Antonelli, Nanometrics, Sean King, Intel Corporation

8:00am **EM-ThM1 John A. Thornton Memorial Award Lecture - PECVD Low and Ultralow Dielectric Constant Materials: From Invention and Research to Products**, ***Alfred Grill***, IBM Research Division, T.J. Watson Research Center **INVITED**

In April this year we celebrated the 50th anniversary of Moore's law which has been followed by the semiconductor industry together with Dennard's scaling law, resulting in continuously improved performance and increased density of the semiconductor microprocessors. For 22 years this was accomplished using the same material composed of Si, Al, O, N, and shrinking the dimensions of the devices. At the 0.25 mm node, the interconnect became the bottleneck to the improvement of the performance of the VLSI integrated circuits and required the introduction of new materials to reduce its RC. After the replacement of Al with the more conductive Cu in 1997, it took seven more years to replace the SiO_2 insulator (k=4) of the interconnect with a low-k dielectric. While the academia and industry were aware already in the 1990s of the need for a low-k dielectric and many potential materials were developed and investigated, none could be integrated in a VLSI product requiring multiple revisions of the. The early, unsuccessful efforts were focused on polymeric or hybrid organic-inorganic films fabricated by spin-on techniques. Realizing that PECVD materials would have superior properties to those of the spin-ons, we invented, developed and characterized the carbon-doped oxide SiCOH, deposited by PECVD, obtaining a material with a dielectric constant k=3 which was successfully integrated in VLSI products starting at the 90 nm node and became the industry standard as the interconnect dielectric. This development has continued with the invention of porous pSiCOH ultralow-k (ULK) dielectrics with further reduced k values. pSiCOH with k as low as ~2 was demonstrated in research lab and a materials with k=2.4 was successfully implemented in products at the 45 nm node, to maintain a reduced capacitance for the scaled dimensions of the shrunken technology nodes.

The talk will discuss the development and optimization of the PECVD SiCOH and pSiCOH dielectrics, integration issues related to these materials of reduced mechanical and chemical properties compared to SiO_2, understanding the correlation between process parameters, dielectric characteristics and the reliability of the integrated interconnect, and the current state of the art of the interconnect dielectrics which enabled the continuation of Moore's law into nanoscale dimensions.

8:40am **EM-ThM3 Moving Across the Periodic Table: Amorphous Hydrogenated Boron Carbide for Low-*k* Dielectric Applications**, ***Michelle Paquette***, *B.J. Nordell, T.D. Nguyen, S.S. Purohit, A.N. Caruso,* University of Missouri-Kansas City*, W.A. Lanford,* University at Albany-SUNY*, P. Henry, S.W. King*, Intel Corporation

A major challenge facing the semiconductor industry is the development of new low-dielectric-constant (low-k) materials for metal interconnects to mitigate the issues surrounding resistance–capacitance (RC) delays as dimensionality is reduced. Such materials include not only bulk inter-/intra-layer dielectrics (ILDs), but also more specialized layers such as Cu diffusion barriers, etch stop layers, and hard masks. Traditional materials for these purposes have been derived from the Si family; however, it is becoming increasingly challenging to tailor these to meet all of the integration requirements, particularly maintaining mechanical and chemical resilience as k is lowered. Toward this end, amorphous hydrogenated boron carbide (a-B_xC:H_y) is an intriguing alternative. Amorphous B_xC:H_y is a unique solid based on six-coordinate icosahedral 'molecular' units. As a semi-insulating low-density solid with one of the lowest possible average atomic numbers, Z (H = 1, B = 5, C = 6), a-B_xC:H_y is expected to feature a low dielectric constant, while also inheriting the appealing properties of crystalline BC, which include extreme hardness, as well as thermal and chemical robustness. We describe novel a-B_xC:H_y materials for low-k ILD, diffusion barrier, and etch stop applications with dielectric constant (<3.5), leakage current ($<10^{-8}$ A/cm^2 at 2 MV/cm), and mechanical properties (Young's modulus >100 GPa) that meet or surpass those of Si-based materials currently being used for these applications. We further explore some of the fundamental similarities and differences between Si- and BC-based classes of materials.

9:00am **EM-ThM4 Enhancing Mechanical and Fracture Properties of ULK Materials with Filled Pores**, *S.G. Isaacson,* Stanford University*, K. Lionti, W. Volksen, T.P. Magbitang,* IBM Almaden Research Center*,* ***Reinhold Dauskardt***, Stanford University*, G. Dubois*, IBM Almaden Research Center

Pore filling has emerged as a promising strategy for the protection of ultra-low-k dielectrics (ULK) against plasma-induced damage [1-3]. In this work we use polymers with a wide range of molecular weights (10^3 – 10^6 g/mol) to create filled ULK materials, leading to uniform penetration, a high level of fill (~100%), and confinement of polymer chains to dimensions far smaller than their bulk radius of gyration. This confinement alters the conformations and inter-molecular interactions of the polymer phase, resulting in novel fracture behavior that has important implications for the reliability of pore-filled ULK materials.

Despite its promise as a processing technique, the effects of pore filling on the mechanical properties, fracture strength, and reliability of these backfilled ULK materials remain poorly understood. We show that the mechanical and fracture properties of a nanoporous ULK matrix can be considerably improved by filling the porosity with a polymeric second phase. Importantly, the degree of toughening increases significantly with the polymer molecular weight, and is also found to depend on processing conditions. We show that the mechanism for toughening is based on the pullout of individual confined polymer chains from the ULK matrix, distinct from the more common entanglement-based mechanisms seen in bulk polymers. This mechanism is quantified with a model that describes the nanomechanical processes occurring on the length scale of individual pores.

Nanoindentation measurements demonstrate that pore filling with confined polymers also improves mechanical properties such as Young's modulus and hardness. Furthermore, we present subcritical crack growth measurements that highlight the mixed effects of pore filling on the moisture-assisted cracking of ULK materials. This study provides new insight into the mechanical behavior of pore-filled ULK materials and suggests potential routes for increasing the cohesive strength of materials where the traditional bulk toughening mechanisms may be absent.

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9:20am **EM-ThM5 Status Update on a New Class of Solution Processable Low-k Dielectric Coatings for Use as ILD with K < 2.4**, ***Hash Pakbaz****, N. Hacker,* SBA Materials*, Z. Tokei, M. Baklanov*, IMEC, KU Leuven Belgium **INVITED**

Liquid Phase Self Assembly (LPSA) is used as a unique approach to create porous carbon-doped SiOx solution processable coatings. In this approach, self assembling organic template, in a solution consisting of various silanes and other additives, form nano-particles. These nano-particles are the basis for pore formation in the final coated film where-by to minimize the over-all energy of the system, the nano-particles tend to maximize their respective distances in solution and during the coating process. Thin films are coated using spin coating and the templates are removed by thermal curing or UV curing the coated film without pore collapse. This leads to formation of "ordered" porous coatings where pore overlap does not occur until high levels of porosity (> 60%) are introduced. As a result, low-k dielectric coatings with k values below 2.0 can be achieved with excellent mechanical properties. In this paper, fundamental properties of LPSA low-k dielectric, integration results in advanced node BEOL dual-damascene structures as well as solution storage lifetime consistent with meeting requirements for production are presented.

11:00am **EM-ThM10 The Effect of Vacuum Ultraviolet Irradiation on TDDB of Low-K Dielectrics using Synchrotron Radiation**, ***Dongfei Pei****, M. Nichols,* University of Wisconsin-Madison*, S.W. King, J. Clarke,* Intel Corporation*, Y. Nishi,* Stanford University*, J.L. Shohet*, University of Wisconsin-Madison

Time-dependent dielectric breakdown (TDDB) is a major concern for low-k dielectrics. Plasma processing, which involves ion bombardment and vacuum ultraviolet (VUV) irradiation, has been shown to cause TDDB degradation of low-k dielectrics. [i] Synchrotron radiation provides high-intensity monochromatic VUV photons with continuous variable wavelength. In this work, synchrotron irradiation between 5 and 20 eV was used to simulate VUV photon irradiation from a plasma without any particle flux. In this work porous organosilicate glass (SiCOH) was irradiated. A Cu / capping layer / SiCOH / titanium stack structure was fabricated so as to analyze the TDDB lifetime of both pristine and VUV-irradiated dielectrics. The photon flux varies with the wavelength so the irradiation time was chosen to produce the same amount of photon fluence at each photon energy. VUV photon energies larger than 7eV were found to create damage to porous SiCOH and cause TDDB degradation. With a photon fluence of 10^{16} photons/cm^2, VUV photons with higher energies tend to cause more TDDB degradation.

This work was supported by the Semiconductor Research Corporation under Contract No. 2012-KJ-2359 and by the National Science Foundation under Grant CBET-1066231.

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11:20am **EM-ThM11 Influence of Porosity on VUV Induced Damage to Low-K Dielectrics**, ***Faraz Choudhury***, University of Wisconsin-Madison*, J.-F. de Marneffe, M. Baklanov,* IMEC, Belgium*, S.W. King,* Intel Corporation*, Y. Nishi,* Stanford University*, J.L. Shohet*, University of Wisconsin-Madison

During various stages of plasma processing, low-k dielectrics are exposed to high levels of VUV radiation emitted from the plasma. Modern ultra-low-k materials have interconnected pores within the dielectric layer that make them susceptible to damage due to their low density and deep penetration of active species into the film. In this work, VUV induced degradation of low-k dielectrics as a function of porosity is investigated. Organosilicate low-k films of porosities between 15% (k=2.7) and 50% (k=1.9) were exposed to synchrotron VUV radiation with energies ranging from 6 -12eV. Both electrical and chemical properties of the films were analyzed to find the most damaging spectral region. FTIR spectra showed increased depletion of the methyl group after VUV irradiation as a function of film porosity and CV measurements showed an increase in the dielectric constant along with a flat-band voltage shift. IV characteristics of the VUV irradiated porous films indicated an increase in leakage currents and lower breakdown voltage. The degree of damage is higher for the more porous films indicating that the introduction of pores deteriorate the electrical properties of the low-k films. The higher leakage currents in the more porous films were attributed to more porogen residues within the dielectric layer. To remove the porogen residues, the films are treated with hydrogen downstream plasma at 300^{O} C. FTIR measurements confirm removal of porogen residues and leakage currents are significantly reduced after the hydrogen-annealing process.

This work has been supported by the Semiconductor Research Corporation under Contract No. 2012-KJ-2359 and the National Science Foundation under Grant No. CBET-1066231.

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11:40am **EM-ThM12 An Electron Paramagnetic Resonance Study of Processing Effects in Porous Low-κ Dielectrics**, ***Michael Mutch***, *P.M. Lenahan,* Pennsylvania State University, *S.W. King*, Intel Corporation

We utilize electron paramagnetic resonance (EPR) to study defects in porous, low-κ SiOC:H powders as a function of processing parameters. The powders were generated by mechanically removing the SiOC:H films from sililcon substrates. The SiOC:H powders studied have previously been investigated after remote hydrogen plasma (RP) and UV cures.[1] To better understand the role of RP and UV curing on defect chemistry, we utilize EPR measurements at each processing step.

First, EPR measurements were performed on a an SiOC:H powder before and after UV treatment. Prior to UV treatment, a spectrum with a zero-crossing *g* of 2.0027 with a line width of 4.5 Gauss is detected. The measured defect concentration prior to UV treatment is about 3x10^{15} cm^{-3}. The zero-crossing *g* suggests a carbon dangling bond defect. Post UV treatment, a carbon dangling bond spectrum is detected with a corresponding defect concentration of 2.1x10^{17} cm^{-3}.[1] The large increase in carbon dangling bond concentration post UV anneal suggests an incomplete removal of the sacrificial porogen resulting in carbon dangling bond defects.

Second, an SiOC:H powder is studied before and after remote hydrogen plasma (RP) and UV treatments. Via fast passage EPR, two overlaying signals are detected prior to RP and UV cures. The two signals are identical in line width and zero-crossing *g* to spectra which have been provisionally attributed to two carbon dangling bond centers termed Cdb1 and Cdb2 by Pomorski et al.[1] Pre RP and UV cure, the measured defect concentrations of Cdb1 and Cdb2 are 2.1x10^{17} cm^{-3} and 2x10^{15} cm^{3}, respectively. Post RP (but prior to UV treatment), the Cdb2 signature is detected and has a defect concentration of 1.8x10^{15} cm^{-3}. The Cdb1 signature, is not detected. This suggests that the hydrogenation of these films via RP is successful in removing some carbon dangling bonds. Post RP and UV cure, a defect with a line width of 11 Gauss and a zero-crossing *g* of 2.0028 is detected at a concentration of 5x10^{17} cm^{-3}.[1] The post UV processed zero-crossing *g* close to that of the free-electron *g* suggests the presence of carbon dangling bond defects. Again, we tentatively attribute these defects to an incomplete removal of sacrificial porogens from the films.

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12:00pm **EM-ThM13 The Effects of VUV Radiation on Low-k Organosilicate Glass (SiCOH) as Measured with Electron-Spin Resonance**, ***Panpan Xue***, *H. Zheng, W. Li,* University of Wisconsin-Madison, *J.-F. de Marneffe,* IMEC, *M. Baklanov,* IMEC, Belgium, *V. Afanas'ev,* Catholic University of Leuven, Belgium, *Y. Nishi,* Stanford University, *J.L. Shohet*, University of Wisconsin-Madison

Here, we investigate the effects of VUV radiation on the defect concentrations in SiCOH. Electron-spin resonance (ESR) spectroscopy is a very effective tool to detect defects in dielectrics. It has been used on various high-k dielectrics, such as HfO_2[1]. In this work, in order to obtain a clear spectroscopic signal, 60nm SiCOH (k=2.4) was deposited on high-resistivity (3000 Ω-cm) wafers. There are at least two kinds of detectable defects in SiCOH: Si dangling bonds (g=2.0054) and Oxygen vacancy (g=2.002). In this work, we concentrate on the silicon dangling bond defects. In order to eliminate dangling bonds from the silicon substrate as well as its edges, CP4 [2] and HF treatments were used. The samples were treated in three ways before ESR (1) CP4 etch that removes surface and edge damage but leaves the SiCOH on the sample. (2) CP4 followed by an HF etch to remove the SiCOH. (3) same as method (2) except here the SiCOH is covered with wax so the HF only etches bare silicon including its edges. Method 3 passivates dangling bonds on the Si surface so any remaining signal should only from the SiCOH. The measurements showed that the sample with SiCOH remaining (method 3) has roughly 1.6 times the number of Si dangling bonds compared with bare Si. In addition, samples having the same edge areas but smaller surface areas were seen to have fewer defects. This shows that the defects measured with ESR are actually from the SiCOH layer but not the edges of the sample. In order to investigate the influence of VUV radiation, the samples were exposed to synchrotron radiation with photon energies of 12 eV for both 10 and 40 minutes. The ESR measurements showed that the defect concentration increased after 10 minutes of VUV exposure and kept increasing with longer VUV exposure times.This is consistent with the fact that the energy threshold for Si-H bond photolysis at the surface of H-passivated Si is ~7.9 eV[3].The ESR signals have a Lorentzian shape and the Bloch model [4] fits these well. We conclude that silicon dangling bond defects in SiCOH and its interface with silicon can be detected using ESR and that VUV exposure increases the defect concentration.

Work supported by the Semiconductor Research Corporation under Contract No. 2012-KJ-2359 and the National Science Foundation under Grant No. CBET-1066231.

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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.

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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.

[1] V. Sidorkin et al., J. Vac. Sci. Technol. B **27**, L18 (2009)

[2] Maas et al., SPIE Proc. **9048**, 90482Z (2014)

MEMS and NEMS
Room: 210B - Session MN-ThM

Atomic Layer Nanostructures and 2D NEMS
Moderator: Tse Nga (Tina) Ng, PARC (Palo Alto Research Center), a Xerox Company

8:00am **MN-ThM1 Piezoelectric and Phase Change Properties of Two-Dimensional Materials**, ***Evan Reed***, Stanford University **INVITED**

Some of the most dramatic accomplishments with 2D materials have been enabled by properties that emerge only at the single or few-layer limit and are not found in bulk forms. Using and developing a variety of atomistic modeling methods, we have predicted that many of the commonly studied single-layer and few-layer transition metal dichalcogenide (TMD) materials (e.g. MoS_2) exhibit substantive electromechanical coupling in the form of piezoelectric and flexoelectric-like effects, unlike their bulk parent crystals.[1] I will describe the first recent observations of some of these effects in the laboratory by several research groups.

Single-layers of two-dimensional Mo- and W-dichalcogenide compounds differ from graphene in an important respect: they can potentially exist in more than one crystal structure. Some of these monolayers exhibit hints of a poorly understood structural metal-to-semiconductor transition with the possibility of long metastable lifetimes. If controllable, such a transition could bring an exciting new application space to monolayer materials. We have discovered that mechanical deformations provide a route to switching thermodynamic stability between a semiconducting and a metallic crystal structure in some of these monolayer materials.[2] Our DFT-based calculations reveal that single-layer $MoTe_2$ exhibits a phase boundary at a few percent tensile strain. The potential application space for this work ranges from information and energy storage to electronic and optical electronic devices.

[1] Karel-Alexander N. Duerloo, Mitchell T. Ong, and Evan J. Reed, Journal of Physical Chemistry Letters **3** (19), 2871 (2012); Karel-Alexander N. Duerloo and Evan J. Reed, Nano Letters (4), 1681 (2013).

[2] Karel-Alexander Duerloo, Y. Li, and E. J. Reed, Nature Communications **5**, 4214 (2014).

8:40am **MN-ThM3 Novel Graphene Devices Based on Laser-Scribing Technology**, *H. Tian,* ***Qian-Yi Xie***, *N.-Q. Deng, L.-Q. Tao, X.-F. Wang, W.-T. Mi, Y.-X. Li, H.-M. Zhao, Y.-T. Li, Y. Shu, Y. Yang, T.-L. Ren*, Tsinghua University, China **INVITED**

Wafer-scale graphene devices could be fabricated by one-step laser-scribing technology. Six kinds of novel graphene devices have been developed, including in-plane transistor, resistive memory, photo detector, earphone, strain sensor and pressure sensor. The in-plane graphene transistor has a large on/off ratio up to 5.34 with simpl e structure. The graphene resistive memory has a Fin-like structure with forming-free, stable switching, reasonable reliability and potential for 2-bit storage. The 1D and 2D arrays of graphene photo detectors were achieved with photo responsivity as high as 0.32 A/W. The graphene earphone realizes wide-band sound generation from 100 Hz to 50 kHz, which can be used for both human and animals. The strain sensor based on graphene micro ribbon has the gauge factor up to 9.49. The sensitivity of the graphene pressure sensor is as high as 0.96 kPa-1 in a wide pressure range (0~50 kPa). These results demonstrated that the laser-scribed technology could be used as a platform to develop novel graphene devices.

Keywords: Graphene Devices; Laser-Scribing; Wafer-scale; Transistors; Memory; Sensors and Actuators

Acknowledgments: This work was supported by National Natural Science Foundation (61434001), 973 Program (2015CB352100), National Key Project of Science and Technology (2011ZX02403-002) and Special Research Fund of Agricultural Science and Technology for Public Interest (201303107) of China.

9:20am **MN-ThM5 Ultrathin Hexagonal Boron Nitride (h-BN) Nanomechanical Resonators**, ***Xu-Qian Zheng***, *J. Lee, P.X.-L. Feng*, Case Western Reserve University

Among recently emerged two-dimensional (2D) materials, hexagonal boron nitride (h-BN) possesses some unique properties, including a wide bandgap (5.9eV) [1] and electrical insulation, excellent thermal stability, and superb inertness [2]. It also has very high elastic modulus (E_Y ~810GPa) which is on the same order with that of graphene [3]. Similar to graphene, h-BN also has very high fracture strain limits [4] that are far beyond achievable values in conventional 3D crystals. In particular, h-BN offers piezoelectricity in an ultrathin 2D platform [5]. Therefore h-BN is an attractive structural material for 2D nanoelectromechanical systems (NEMS), especially as resonant transducers in harsh environment applications.

In this work, we describe the construction of h-BN drumhead structures and the first demonstration of vibrating h-BN 2D NEMS resonators. We investigate the elastic properties and resonant characteristics of such devices, by measuring flexural-mode resonances using ultrasensitive laser interferometry. We first fabricate circular drumhead h-BN resonators with thickness ranging from 9nm to 292nm and diameter of ~10μm using a completely dry transfer technique [6]. Then, by conducting both undriven and driven measurements on h-BN resonators, we observe and study the multimode resonances up to 7 modes, in high frequency (HF) and very high frequency (VHF) range. We further conduct spatially resolved measurements to attain the mode shapes of the multimode resonances. We then investigate the multimode frequency scaling of h-BN nanomechanical resonators with different thickness and analyze the experimental results to extract the elastic properties, structural and geometric effects. Finally, in comparison with the previously studied graphene and MoS_2 2D NEMS resonators, we identify potential applications of these new h-BN devices in the 2D NEMS family.

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[2] A. Pakdel, *et al.*, *Chem. Soc. Rev.* **43**, 934-959 (2014).

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

[4] L. Song, *et al.*, *Nano Lett.* **10**, 3209-3215 (2010).

[5] K.-A. Duerloo, *et al.*, *J. Phys. Chem. Lett.* **3**, 2871-2876 (2012).

[6] R. Yang, *et al.*, *J. Vac. Sci. & Tech. B* **32**, 061203 (2014).

9:40am **MN-ThM6 Microfabricated MoS_2 and MoS_2/Graphene Aerogel based Sensor for NO_2 Gas Detection**, ***Hu Long***, University of California at Berkeley, *M. Worsley,* Lawrence Livermore National Laboratory*, A. Harley-Trochimczyk, C. Carraro, R. Maboudian*, University of California at Berkeley

Two dimensional layered materials, such as graphene and transition metal dichalcogenides (TMD) have great potential for gas sensing applications. Ultrasensitive chemical detection using single-layer graphene and single- and few-layer MoS_2 has been reported. However, many of these sensors suffer from slow response and recovery. The difficulty of the fabrication process also hinders the broader application of these materials. In this paper, we report on MoS_2 and MoS_2/graphene aerogels for chemical sensing applications. The aerogels are integrated onto a microfabricated transducer and a ppb level detection limit for NO_2 at room temperature is achieved. The performance of the sensors is comparable to the results reported for single or few-layer MoS_2 devices but follows much more scalable synthesis and device fabrication processes.

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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[3] W. Volksen, K. Lionti, T. Magbitang, G. Dubois, *Scripta Mater.*, 2014, 74, 19-24.

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 ($2x10^{16}$ cm^{-2}) results a relatively high Si concentration obtaining at the implanted maximum of $5.3x10^{21}$ 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 $\sim 10^{-9}$ 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 micro-device. 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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Plasma Science and Technology
Room: 210A - Session PS+2D-ThM

Plasma Processing for 2D Materials
Moderator: Eric Hudson, Lam Research Corporation

8:00am **PS+2D-ThM1 Low Pressure Plasma Cleaning and Doping of CVD Graphene**, ***Daniil Marinov***, LPP-CNRS, Ecole Polytechnique, France, *G. Cunge*, LTM - CEA/LETI, France, *D. Ferrah*, CEA, LETI, MINATEC Campus, France, *E.V. Johnson*, LPICM-CNRS, Ecole Polytechnique, France, *J.-P. Booth*, LPP-CNRS, Ecole Polytechnique, France **INVITED**

The rising importance of graphene and other 2D materials presents interesting new challenges for plasma technology. Processing of atomically thin layers requires unprecedented control of plasma parameters such as the fluxes and energy distributions of both ions and neutrals at the substrate. With sophisticated control, plasma technology can offer solutions to the major technological bottlenecks associated with graphene applications. Polymer residues (originating from the transfer of CVD graphene or from photo-resist masks) uncontrollably alter the electronic and chemical properties of graphene, a major problem for graphene integration in sophisticated devices. Removal of these surface contaminants by selective hydrogen plasma etching can perform better than classical techniques (wet chemistry with annealing) in terms of efficiency, throughput and compatibility with device fabrication processes [1]. In order to avoid plasma induced damage during graphene cleaning, the ion energy must be kept low (e.g. below 12 Ev for H+ ions [2]). Band gap opening in graphene is another major challenge that can be tackled by plasma doping, provided that the ion energies can be controlled to favor substitutional doping rather than sputtering [3].

We are evaluating two types of plasma reactors for controllable cleaning and doping of graphene – a low density capacitive discharge excited by non-sinusoidal tailored voltage waveforms (TVW) and a high density pulse-modulated inductive plasma source. Both systems are capable of generating hydrogen plasmas with sufficiently low ion energies for low damage residue cleaning. The polymer (PMMA) etch rate obtained in the high density ICP is two orders of magnitude higher, making this system more suitable for graphene cleaning. The TVW discharge is particularly interesting for graphene doping. By changing the excitation voltage waveform in nitrogen CCP one can control the ion bombardment energy and hence the binding configuration of N dopants in single layer graphene. Using an ion bombardment energy of about 40 Ev nitrogen atoms can be incorporated with a total concentration of 5 at. %, with more than half of them in graphitic sites. When the ion energy is below 20 Ev only pyridinic and pyrrolic N is observed.

The role of the substrate carrying the graphene was found to be very important. In the case of hydrogen plasma treatment, ions passing through the graphene layer may participate in catalytic reactions at the substrate or lead to blister formation.

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[2] Despiau-Pujo *et al.J.Appl.Phys. 2013, 113,114302*

[3] Zhao *et al.Phys. Rev. B* 2012, 86, 165428

8:40am **PS+2D-ThM3 Sensing Cleanliness of PMMA Transferred CVD Grown Graphene**, ***Christian Teichert***, *M.C. Kratzer*, Montanuniversität Leoben, Austria, *B.C. Bayer*, University of Cambridge, UK

Crystalline films of small organic semiconductors offer attractive potential for optoelectronic applications on flexible substrates. However, these applications require a transparent and flexible electrode material; and here the novel material graphene (Gr) comes into play. Since small conjugated molecules like the rod-like oligophenylene molecule para-hexaphenyl (6P) fits well to the hexagonal structure of graphene, growth of 6P on Gr can be expected in a lying configuration.

As demonstrated by in situ by low-energy electron microscopy, 6P grows at 240 K indeed in a layer-by-layer mode with lying molecular orientation on Ir(111) supported graphene [1]. Islands nucleate at Gr wrinkles [2]. At higher temperatures, needle-like 6P crystallites - also composed of lying molecules are observed [3]. Also on exfoliated, wrinkle-free graphene, such needles develop with discrete orientations defined by the Gr lattice as was detected by atomic-force microscopy (AFM) [4,5]. Needles are never observed on contaminations or on the silicon oxide substrate. There, exclusively islands composed of upright standing molecules are observed. Since these islands are easily detected by AFM, growth of 6P can be used to sense the cleanliness of a variety of graphene substrates as we have demonstrated for PMMA transferred CVD grown graphene. On the as grown samples, PMMA remainders hinder the growth of extended needles. For increasing anneling temperature, the 6P needles grow in length because the PMMA residues decrease substantially [6].

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9:00am **PS+2D-ThM4 Plasma Processes of Graphene and Related 2d Materials for Energy Applications**, *L.C. Chen*, ***Indrajit Shown***, National Taiwan University, Taiwan, Republic of China **INVITED**

Plasma-assisted direct-growth of arrayed graphene and related hybrids will be presented. The main advantages of this type of nanostructures include high conductivity, high surface area and corrosion resistance, making them excellent candidates as electrocatalytic supports or electrodes for electrochemical (EC) energy applications, including fuel cells, supercapacitors and solar fuels. We will demonstrate the fabrication of integrated energy devices in an on-chip manner. Since the carrier transfer rate of electrode plays a crucial role in determining the energy-conversion performance, special emphases will be placed on the control of interfaces. Vertically aligned and edge-oriented graphene arrays were first synthesized by microwave plasma-enhanced chemical vapor deposition. Subsequent chemical doping can also be done in the same plasma reactor via either in-situ or ex-situ manners. Interestingly, for nitrogen doping in graphene, plasma process resulted in selective bond configuration. When applied as an EC electrode, the arrayed graphene exhibits nearly reversible redox characteristics. By varying the process parameters, samples can be produced with controllable compressive or tensile strains, which in term show strong effects on the resultant catalytic properties.

The hierarchical graphene nanowalls can be directly grown on a variety of substrates, including Si wafers, carbon cloth as well as flexible and ultralight carbon nanofibers. The latter substrate makes such electrode an ideal portable platform having high gravimetric, areal, and volumetric electrochemical characterizations. For instance, the carbon nanofibers supported graphene-based supercapacitors exhibit excellent specific capacitance of 352.53 F/g (220.33 mF/cm^2) at a specific current of 13.33 A/g, which is among the highest reported to date. Meanwhile, 99 % of Coulomb efficiency and 98 % of the initial capacitance after 10,000 charge-discharge cycles were maintained. Finally, efficient and simple routes to further attach other heterogeneous nanostructures onto graphene nanowalls have also been developed. Cyclic voltammeter studies for electro-oxidation of methanol show a high ratio of forward anodic peak current to reverse peak current, suggesting an efficient oxidation of methanol to CO_2 on the graphene-based electrode. Our approach offers a promising route toward wafer-scale fabrication of graphene not only for fundamental research but also opens up various potential applications in sensing, catalysis, as well as energy storage and production.

11:00am **PS+2D-ThM10 Engineering Chemical Functionality in Graphene**, ***Sandra Hernandez***, *P.E. Sheehan, S. Tsoi, P. Dev, J.T. Robinson, C. Junkermeier, K.E. Whitener, W.K. Lee, T.L. Reinecke, S.G. Walton*, Naval Research Laboratory

Graphene has attracted enormous attention due to its unique properties. Equally important is the ability to further tailor these properties through modification of select attributes such as surface chemistry, number of layers, sheet width, and edge structures. Manipulating the surface chemistry of graphene is important since the chemical composition strongly impacts the electronic properties as well as chemical reactivity both globally and locally. Precise control of the surface chemistry of graphene can also allow for subsequent surface procedures focused on band gap engineering, device fabrication and sensor applications. Given the strong impact of adsorbates, global chemical modification provides opportunities towards greater control over the properties of graphene films. Control over the spatial distribution of these groups provides an even greater functionality in that the local graphene reactivity can be manipulated, opening up a wealth of opportunities in biosensing, plasmonics, catalysis, smart surfaces, and heterojunction devices.

Using the unique attributes of electron beam generated plasmas to manipulate the chemistry of graphene and employing patterning techniques to regulate the spatial distribution of various functional groups on the surface, we demonstrate further abilities to govern surface properties. Spatial control over structural and chemical changes is characterized through micro (m-Raman and high-resolution x-ray photoelectron spectroscopy (XPS) mapping and electrical measurements are used to determine how local changes in chemistry influence the electronic properties. Lastly, we show that the resulting chemical moieties can be used to manipulate the local surface reactivity of graphene, enabling programmable, site-specific electrochemical deposition. These findings demonstrate the ability to tailor the locality of the surface chemistry on graphene surfaces opening up a wide range of reactivity studies and synthesis capabilities, such as programmable material deposition.

11:20am **PS+2D-ThM11 Formation of Aromatic Nitrogen Groups in Graphene Films by Post-Growth Treatment in Late-Afterglows of Nitrogen Microwave Plasmas**, ***Luc Stafford***, Universite de Montreal, Canada

Graphene films were exposed to the late afterglow of a reduced-pressure N_2 plasma sustained by microwave electromagnetic fields. X-ray photoelectron spectroscopy (XPS) shows that plasma-generated N atoms are incorporated into both pyridinic and pyrrolic groups, without excessive reduction of sp^2 bonding. Nitrogen incorporation was found to be preceded by N adsorption, where N adatom density increased linearly with treatment time while aromatic nitrogen saturated. This finding was confirmed by Raman spectra showing a linear increase of the D:G ratio attributed to constant surface flux of plasma generated species.

Combined Density Functional Theory calculations with a Nudged Elastic Band (DFT-NEB) approach indicate that incorporation reactions taking place at point vacancies in the graphene lattice requires an activation energy in the 2-6 eV range, but the energy required for the reverse reaction exceeds 8 eV. Stable nitrogen incorporation is therefore judged to be defect-localized and dependent on the energy transfer (6 eV) provided by $N_2(A)$-to-$N_2(X)$ metastable-to-ground de-excitation reactions occurring at the late-afterglow-graphene interface.

Selective Deposition as an Enabler of Self-Alignment Focus Topic
Room: 210F - Session SD+AS+EM-ThM

Fundamentals of Selective Deposition
Moderator: Scott Clendenning, Intel Corporation, Suvi Haukka, ASM Microchemistry Ltd., Finland

8:00am **SD+AS+EM-ThM1 Fundamental Examinations of Surface Chemistry-Driven Approaches to Selective Area Atomic Layer Deposition**, *W. Zhang, J.-R. Chen, **James Engstrom***, Cornell University

Most approaches taken to date concerning selective area growth have involved the use of masking layers consisting of photoresists or self-assembled monolayers (SAMs). While some success has been achieved with this approach there are a number of disadvantages intrinsic to these methods. First, SAMs are very difficult to form defect free, and second, and perhaps more important, these masking layers themselves must be patterned or deposited selectively. A second approach to selective area ALD relies on intrinsic reactivity differences between exposed surfaces, which, unfortunately, may be limited to a few special cases. Here we seek to develop a more general approach to achieving selective area growth. We initially focus on the first half-cycle of ALD, where demonstrating selectivity for this part of the ALD process is a necessary, but not sufficient condition for selective area growth. We are examining two specific approaches to the surface chemistry: (*i*) the use of adsorption reversal agents; and (*ii*) the use of molecular blocking agents. Here for a thin film precursor we examine transition metal complexes with the generic structure, $M(XR_m)_n$, where M is the transition metal and XR_m is the coordinating ligand. In pursuing strategy (*i*) we examine the introduction of a second species in the first half-cycle that can act as a coordinating ligand, e.g., HXR'_m, or $HXR'_{m-1}R''$, etc. In pursuing strategy (*ii*) species (Y) are selected that can effectively compete for adsorption sites, dependent on the composition of the substrate. Concerning strategy (*i*) we are currently investigating reactions between transition metal amido compounds and a series of amines ($X = N$). We have found a somewhat unexpected result for this chemistry: the partial pressure of H_2NR' produces similar effects on both a metal (Cu) and a dielectric (SiO_2) surface, where a low partial pressure attenuates the irreversible adsorption of the thin film precursor, while a high partial pressure results in no adsorption of the precursor. An investigation of the reactions between the thin film precursor and a molecular blocking agent with the structure HSR'', gave much more encouraging results. Here we found complete blockage of chemisorption of the thin film precursor on a Cu surface, whereas on SiO_2 the molecular blocking agent had no effect on the adsorption of the metal for the first half-cycle. We will conclude this presentation with a discussion of the mechanisms that are likely operative in both cases, making use of *in situ* measurements involving X-ray photoelectron spectroscopy, and also initial results concerning the effectiveness of this approach for multiple (5-20) cycles of ALD.

8:20am **SD+AS+EM-ThM2 Mechanistic Understanding of Surface-Selective Chemical Vapor Deposition of Copper Films Using a Molecular Inhibitor**, ***Elham Mohimi**, S. Babar, B. Trinh, G.S. Girolami, J.R. Abelson*, University of Illinois at Urbana Champaign

Surface-selective chemical vapor deposition of thin films can enable the fabrication of nanoscale devices by eliminating difficult patterning and etching steps. However, stray nucleation of film on the non-growth surface due to defect or impurity sites remains a challenging problem. We previously demonstrated the use of molecular growth inhibitors in copper CVD to control morphology, ranging from a smooth and continuous thin film to particles in a narrow size distribution. Here, we show that an inhibitor can also be used to afford essentially perfect selective growth. Addition of vinyltrimethylsilane (VTMS) molecules during copper CVD from the Cu(hfac)VTMS precursor reduces the growth rate of copper on copper by a factor of four, but reduces the Cu deposition on thermal SiO_2 or porous carbon doped SiO_2 to below one monolayer (area averaged). In-situ FTIR and mass spectroscopy show that the VTMS undergoes associative desorption with adsorbed Cu(hfac) intermediate on the non-growth surface, and is responsible for the surface selective deposition of copper only on the intended (metallic) substrate areas. The processing window for this method is wide in terms of VTMS pressures (> 1 mTorr), growth times (1-90 min), and substrate temperature (100-180°C).

8:40am **SD+AS+EM-ThM3 Selective Deposition of Copper-Manganese Alloy for Interconnects**, ***Roy Gordon***, Harvard University **INVITED**

As copper interconnections are made smaller, they fail more easily by electromigration. The dominant pathway for motion of Cu atoms is along the interfaces between Cu and the surrounding insulator surfaces. In current technology, a tantalum nitride diffusion barrier and a Ta or Co adhesion layer are placed between Cu and the insulators. Because these layers are more resistive than Cu, the composite interconnect line has a higher resistance than one that would consist entirely of pure Cu. Here we describe how selective placement of manganese within the insulator surface can provide the necessary stabilization, adhesion and barrier properties for Cu lines without the resistance penalty of TaN/(Ta or Co) layers. After trenches and vias are etched into the insulator, CVD is first used to deposit a thin layer of manganese nitride conformally on all exposed surfaces of the insulator as well as on the Cu exposed at the bottoms of the vias. Then less than a monolayer of iodine is chemisorbed onto the MnN_x from ethyl iodide vapor. Next, this iodine catalyzes selective, bottom-up CVD of Cu-Mn alloy so that it fills even the narrowest trenches and vias without any voids or seams at the centerlines. The iodine "floats" on the growing surface of the Cu, and is finally removed by chemical-mechanical polishing along with the Cu-Mn overburden and the MnN_x on top of the insulator. During subsequent anneals, Mn rapidly diffuses out from the MnN_x and from the Cu-Mn alloy into the near-surface regions of the insulator to form an insulating layer of $MnSi_xO_yN_z$ surrounding the Cu. The necessary Cu adhesion and barrier properties are provided by this insulating layer of $MnSi_xO_yN_z$ selectively placed just inside the surfaces of the insulators. During anneals, Mn and nitrogen originally located on the Cu surfaces at the bottoms of vias disappear as the Mn and N are re-distributed by diffusion to nearby insulator surfaces. The result is direct, low-resistance connection between Cu in vias with Cu in the metallization level below. This selective migration of Mn leaves pure, low-resistance Cu completely filling the entire volume of trenches and vias, providing the lowest possible line resistance. Thus Mn is placed selectively only where it is required to increase adhesion and lifetime before failure by electromigration, to prevent diffusion of Cu into the insulator and to avoid corrosion of Cu by water or oxygen. The same sequence of process steps can apply Cu to the walls of through-silicon-vias to conduct signals from one chip to another. This process can also form Cu seed layers for electrodeposition of Cu-filled vias for distributing power through silicon chips.

9:20am **SD+AS+EM-ThM5 Selective Growth of First Row Transition Metal Films by Atomic Layer Deposition**, ***Charles Winter***, Wayne State University **INVITED**

Our laboratory seeks to develop the growth of metallic first row transition metal thin films using atomic layer deposition (ALD). The microelectronics industry is calling for the growth of metallic first row transition metal films by the ALD method for a variety of applications, including copper metallization, seed layers for copper metallization, copper/manganese alloys for self-forming copper diffusion barriers, and magnetic alloys. The ALD growth of noble metal thin films has been explored extensively in the past ten years, due to the positive electrochemical potentials of these metal ions and relative ease of reduction to the metallic state. The low temperature ALD of high purity, low resistivity Cu films has been described, but ALD routes to the other metallic first row transition metal films remain poorly developed, largely because of the negative electrochemical potentials of most of the ions and a corresponding lack of powerful reducing co-reagents that can convert precursors in positive oxidation states to the metals. We will describe the synthesis, structure, and properties of a large series of new first row transition metal ALD precursors containing alkoxide ligands that combine high volatilities, high thermal stabilities, and high reactivities toward reducing agents. We will also report borane reducing agents that can react with the metal precursors to afford metallic films. Additionally, we will overview the thermal growth of metallic copper, nickel, cobalt, iron, manganese, and chromium thin films from these new precursors. Importantly, the growth of these metals is highly selective for noble metal substrates, such as ruthenium, palladium, and platinum. The noble metal substrates appear to activate the borane reducing agents, thus enabling selective metal growth. Chemical insights into the selective growth will be presented.

11:00am **SD+AS+EM-ThM10 Etching and Chemical Functionalization of Silicon Nitride Surfaces for Selective Deposition**, *L.-H. Liu, T. Peixoto, W. Cabrera, D. Dick, J.-F. Veyan,* University of Texas at Dallas, *D.J. Michalak, R. Hourani,* Intel Corporation, *M.D. Halls,* Schrodinger, Inc., *S.P. Pujar, H. Zuilhof,* Wageningen University, Netherlands, ***Yves J. Chabal***, University of Texas at Dallas

The ability to process silicon nitride and oxide films and chemically functionalize their surfaces by wet chemical methods is critical for selective deposition. The nature of HF-etched silicon nitride surface is complex and somewhat controversial. We have therefore performed an extensive study of HF etching of both Si_3N_4 and SiO_2 surfaces, combining spectroscopic techniques (Infrared absorption, X-ray photoemission, Low energy ion scattering), imaging (atomic force microscopy) and contact angle measurements with first principles calculations, as a function of HF concentration. We have also performed post-treatment in cold and hot water, and chemical functionalization with a range of organic molecules to help determine the chemical nature of the HF-etched surfaces.

The nature of silicon nitride surfaces is complex. We find that immediate rinsing in deionized water after HF wet-chemical etching yields smooth silicon nitride surfaces with clear evidence for Si-F surface termination. Low energy ion scattering experiments and XPS measurement as a function of gentle sputtering with Gas cluster ion beams (GCIB) confirm that the F is all located at the surface (i.e. not distributed into the bulk), and in the form of Si-F with high temperature stability (up to 600 ^{o}C in ultra-high vacuum). Hydrolysis in water is very slow at room temperature, but can be achieved at high temperature (~90 % removal at 70 ^{o}C for 30 min). However, water is found to etch silicon nitride, as evidence by a loss of Si_3N_4 phonon absorption, suggesting that the removal of the surface fluorine may not only be due to surface reaction through a direct exchange mechanism via pentavalent Si intermediate, but also to the hydrolyzation of Si_3N_4 itself through back-bond chemical attack by water. In addition to F, we find that there is also surface $-NH_2$ species, as evidenced by IR active $-NH_2$ bending modes at 1550 cm^{-1}, which we estimate to be only ~20 % monolayer from analysis of reaction with aldehyde molecules. However, this coverage appears sufficient to protect the Si_3N_4 surface. Finally, LEIS and XPS indicate that there is oxygen at the surface, which could either be in the form of -OH or Si-O-Si. Functionalization with alkylsiloxanes reveals that ~50 % of the surface contains Si-OH. In summary, the sum of the concentrations (50 %, 20 %, 50 % in ML), i.e. exceeding 1 ML, suggests that the etched surface may be atomically rough. Overall, these findings provide a method for selective deposition by using first aldehyde reaction for Si_3N_4 functionalization, followed by silane reaction for SiO_2 functionalization.

11:20am **SD+AS+EM-ThM11 Area Selective Deposition of Ultrathin Magnetic Cobalt Films via Atomic Layer Deposition**, ***John Ekerdt***, *H. Nallan, T. Ngo, S. Chopra, Z. Zhang*, University of Texas at Austin

Ferromagnetic thin films find applications in a variety of fields, such as electronics, spintronics, RF technology, energy, etc. With ever-decreasing device feature sizes, film conformity and crystalline structure become very important to determining magnetic properties. As such, atomic layer deposition (ALD) is a very attractive technique for magnetic film deposition as it ensures atomic level conformity. Since ALD film growth necessarily involves a film nucleation step, it is possible to engineer the surface energy of the substrate to cause preferential wetting and nucleation in only desired areas, resulting in area selective ALD (AS-ALD). Unlike conventional photolithography-based fabrication, a bottom-up patterning approach could eliminate the need for etch steps, reducing the cost of fabrication and overcoming scaling limitations in manufacturing devices. This work investigates the selective deposition of cobalt oxide via ALD that is subsequently reduced to carbon-free cobalt metal for use as the free magnetic layer within the magnetic tunnel junction of spin-transfer torque random access memory.

Alkylchlorosilanes and poly(trimethylsilylstyrene) are utilized to block water and cobalt bis(N-tert butyl, N'-ethylpropionamidinate) from an oxide substrate, such as silicon dioxide, hafnium dioxide and magnesium oxide, ensuring selective deposition of CoO films. Poly(trimethylsilylstyrene) is the half of a lamellar forming diblock copolymer that remains after self-assembly and feature development. The alkylchlorosilanes can be blanket deposited through the vapor phase or stamped onto the oxide surface using a poly(dimethylsiloxane) stamp. Cobalt oxide ALD proceeds on the exposed oxide surface. Strontium and Al are deposited atop the CoO films to scavenge oxygen during thermal annealing to yield cobalt metal films. Alternatively, reducing gases such as CO and H_2 can be employed as an oxygen sink during thermal reduction of CoO to Co metal. Finally, we demonstrate control over the tunability of the coercivity of the resultant films by controlling the reduction conditions.

11:40am **SD+AS+EM-ThM12 Area-Selective Al_2O_3 Pattern Grown by Atomic Layer Deposition**, ***Seunggi Seo***, *H. Jung, I.K. Oh, H. Kim,* Yonsei University, Republic of Korea, *J. Yoon, C. Yoo, H.-J. Kim, Y.-B. Lee*, LG Display Co., Ltd., Republic of Korea

Over many past years, area-selective atomic layer deposition (AS-ALD) has been developed for fabricating 3D nanostructures. ALD is a method to deposit thin films by self-limiting surface reactions between supplied gaseous precursors. Since ALD is a surface sensitive deposition technique, surface modification of substrate renders the deposition of films to be area-selective. Most previous studies on AS-ALD have utilized self-assembled monolayer (SAM), which inhibits the chemical reaction between substrate and precursors, so that the film cannot grow on SAM-coated area. AS-ALD has been studied on various materials, such as TiO_2, ZnO, and HfO_2. Although Al_2O_3 has been widely used for ALD, there is no experimental report on AS-ALD Al_2O_3 by using SAM. Rather, a previous report on the calculation of surface reactions between TMA and SAM by density functional theory (DFT) has been presented[1]. That paper describes that CH -terminated SAM shows no thermodynamic driving force for the reaction between them, leading to AS-ALD Al_2O_3 by using TMA.

In this work, we systematically investigated AS-ALD of Al_2O_3 on SAM in various conditions, such as SAM coating methods, the kinds of SAM and substrate, and ALD process parameters. Addressing previous calculation report, Al_2O_3 was deposited on CH_3-terminated SAM, octadecyltrichlorosilane (ODTS) and octadecylphosphonic acid (ODPA).

However, we observed Al_2O_3 layers were formed on SAM coated SiO_2 and Ti substrate, which is inconsistent with previous report. To clarify, we investigated ALD Al_2O_3 on SAM coated substrate by using various analytic techniques such as contact angle measurement, Fourier transform infrared spectroscopy, ellipsometry, X-ray photoelectron spectroscopy (XPS), X-ray-reflectometry (XRR), and α-scanning. We observed TMA was physisorbed on CH_3-terminated SAM, leading to Al_2O_3 deposition. Alternatively, we moved to our research toward the change of SAM coating methods, dipping and stamping, to lift both Al_2O_3 and underneath SAM coating off. Since stamping method is a faster process than dipping one, so that SAM by stamping might remain randomly distributed as forming weak bonding between SAMs and substrate. Moreover, we chose ODPA as a SAM due to its poor adsorption on SiO_2. We observed that both Al_2O_3 and its underneath ODPA stamped on SiO_2 were lifted-off from the substrate, resulting in area-selective Al_2O_3 pattern. This result opens a new way to patterning techniques for many areas of technology.

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Surface Modification of Materials by Plasmas for Medical Purposes Focus Topic
Room: 211D - Session SM+AS+BI+PS-ThM

Plasma Processing of Biomaterials
Moderator: Deborah O'Connell, University of York, UK, Satoshi Hamaguchi, Osaka University, Japan

8:00am **SM+AS+BI+PS-ThM1 Potential of Low Temperature Plasma Sources in Cancer Treatment**, ***Jean-Michel Pouvesle***, GREMI CNRS/Université d'Orléans, France, *G. Collet,* CNRS, *E. Robert,* GREMI CNRS/Université d'Orléans, France, *L. Ridou,* CNRS-CBM, France, *S. Dozias, T. Darny,* GREMI CNRS/Université d'Orléans, France, *B. El Hafni-Rahbi, C. Kieda*, CNRS-CBM, France **INVITED**

The last decade has seen an impressive increase of the research dedicated to the biomedical applications of low temperature Non Thermal Plasmas (ltNTP), especially with plasma sources working at atmospheric pressure. Medical applications of ltNTP now concern a very wide range of domains including cancer treatment. The antitumor effect of ltNTP has been clearly shown *in vivo* on murine modelswith various cancer types (bladder, colon, glioblastoma, melanoma, ovary, pancreas). Although the involved mechanisms are far from being fully understood, the therapeutic effect is now totally admitted and the first clinical study (head and neck) has been reported [1]. In case of plasma jet experiments, the observed effect are most of the time attributed to the very rich chemistry generated by the interaction of the rare gas plasma plume with the surrounding environment constituted either from the ambient air, or this latter in complex interaction with liquids at the interface with the targeted organ. Our recent experiments performed on tissue oxygenation[2] or breast cancer treatments on immunocompetent mice [3] lead to the conclusion that probably the involved chemistry couldn't, alone, completely allow describing the observed phenomena. This, especially under very soft treatment conditions, is suggesting possible triggering of some immune system chain processes and also possible modifications in the microenvironment of tissue and tumors. In this context, there is still an unknown role of the electric field associated with the ionization front or generated in the environment of the plasma plume tip. Taking into consideration the recent vessel normalization based-cancer treatment, the ltNTP effect should be further investigated in view of blood vessels structure and function (blood flow) as well as tumor hypoxia compensation to confirm a possible ltNTP-based adjuvant approach for cancer treatments. These results suggest new ways, especially combined therapy, to consider the plasma and its therapeutic delivery in ltNTP-based tumor therapy. In this talk, after a presentation of the context and the plasma devices, we will go through the specific case of cancer treatment with what have been already demonstrated *in vitro* and *in vivo*, what can be directly linked with the produced discharges, including recent results on electric field measurements in plasma biological application conditions.

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[2] G. Collet *et al* PSST **23** (2014) 012005

[3] G. Collet *et al* ICPM5, May 18-23, 2014, Nara (Japan)

8:40am **SM+AS+BI+PS-ThM3 Plasma Polymerized Polypyrrole Thin Films and Their Use in Drug Release Control**, *C. Li,* National Yang Ming University, Taiwan, Republic of China*, **Yung Te Lee**,* National Central University, Taiwan, Republic of China*, J.H. Hsieh*, Ming Chi University of Technology, Taiwan, Republic of China

Polypyrrole thin films were deposited using a plasma polymerization process. During deposition, power input (between 30W to 70W), monomer (pyrrole) flow rate (30 sccm to 50 sccm), and Ar flow rate were varied. Optical emission spectroscopy (OES) was used to study the plasma characteristics under each deposition condition. After deposition, these films were characterized using FTIR, AFM, ellipsometry, ultraviolet–visible (UV–vis) spectroscopy, and surface profilometer. Eventually, these films were applied to control drug release rate under different thickness and structure. The results were correlated with the process parameters and plasma conditions.

9:00am **SM+AS+BI+PS-ThM4 Thin Film Metallic Glass: A Novel Coating for Various Biomedical Applications***, **Chia-Chi Yu**, Y. Tanatsugu, S. Chyntara, C.M. Lee, W. Diyatmika, J.P. Chu,* National Taiwan University of Science and Technology, Taiwan, Republic of China*, M.J. Chen, S.H. Chang, W.C. Huang*, Mackay Memorial Hospital Tamsui Campus, Taiwan, Republic of China

Thin film metallic glasses (TFMGs) exhibit unique properties such as high strength, smooth surface as well as good wear- and corrosion-resistances due to their amorphous atomic structure. The biocompatibility and antibacterial property of TFMGs can also be obtained, which show great potential for biomedical applications. In addition, the low surface free energy of TFMGs in certain compositions can be achieved and leads to the relatively high hydrophobicity and the low friction coefficient.

In this presentation, various applications of TFMG are discussed, including the property enhancements of dermatome blade and syringe needle, thrombosis reduction for intravenous catheter, and the suppression of cancer cell attachments. A Zr-based TFMG is coated on substrates by using magnetron sputtering. The TFMG-coated dermatome blade show a great enhancement of durability and sharpness, compared with those of the bare one. For the syringe needle, significant reductions in insertion and retraction forces for TFMG-coated needle are achieved due to the non-sticky property and relatively low coefficient of friction. For thrombosis reduction, less platelet aggregations are observed on the TFMG than that on the bare glass in platelets adhesion test, suggesting TFMG-coated catheters is potentially useful to be placed into vessels for long periods of time with reduced numbers of the aggregation of blood platelets. For cancer cell attachment suppressions, TFMG exhibits the least cancer cell attachment among other control groups. Thus, anti-proliferation and anti-metastasis of medical tools can be achieved with TFMG coating.

9:20am **SM+AS+BI+PS-ThM5 Plasma Surface Functionalization of Nano-structured Materials for Biomedical Applications**, ***Masaaki Nagatsu**, H. Chou, A. Viswan, T. Abuzairi, M. Okada, M.A. Ciolan,* Shizuoka University, Japan*, N.R. Poespawati, R.W. Purnamaningsih,* University of Indonesia*, A. Sakudo,* University of the Ryukyus, Japan*, S. Bhattacharjee*, Indian Institute of Technology, Kanpur, India **INVITED**

In this study, we will present the recent experimental results on plasma surface functionalization of nano-structured materials for bio-medical applications.

First, with the graphite-encapsulated magnetic nanoparticles(MNPs), we studied the surface functionalization by using the Ar plasma pre-treatment followed by NH_3 plasma post-treatment, to introduce the amino groups onto the surface of the nanoparticles.1) The amino group population of each nanoparticle with a typical diameter of 20 nm was evaluated by using the conventional chemical technique using SPDP and DTT solutions and we obtained about 8 x 10^4 amino groups per nanoparticle.2) Immobilization of the antibody of influenza virus onto the surface of amino-modulated magnetic nanoparticles was then performed for aiming at studying the feasibility of collection and condensation of virus. After magnetic separation, we succeeded in a significant concentration of the influenza virus number compared with that of the initial sample.3) Using the same method, we also demonstrated a higher concentration of Salmonella about 70 times higher than that of initial sample by the magnetic separation.4) The present results suggest the feasibility of the proposed plasma surface functionalized MNPs for rapid concentration of influenza virus or various bacteria.

As the second topic, the selective ultrafine surface modification of functional groups onto the polymeric substrate or vertically aligned CNT dot-array with a dot size of several μm was investigated using the atmospheric pressure plasma jet with a nano/micro-sized capillary. The micro-sized surface modification of amino or carboxyl groups introduced onto the CNT dot-array were confirmed by the fluorescence labelling technique.5) With fluorescence-labeled avidin molecules, we also confirmed efficient capturing of avidin molecules by the biotin-immobilized CNT dot array through strong biotin-avidin binding process. The present result supports the feasibility of future biochip sensor to detect specific protein, virus or bacteria. In addition to these results, the other experimental results will be presented and discussed at the conference.

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11:00am **SM+AS+BI+PS-ThM10 Tailoring Biomaterials-cell Interaction through Reactive Surface Modification**, ***Salvador Borros***, Institut Químic de Sarrià, Ramon Llull University, Barcelona, Spain **INVITED**

The immobilization of biologically active species is crucial for the fabrication of smart bioactive surfaces. For this purpose, plasma polymerization is frequently used to modify the surface nature without affecting the bulk properties of the material. Thus, it is possible to create materials with surface functional groups that can promote the anchoring of all kinds of biomolecules. Different methodologies in protein immobilization have been developed in recent years, although some drawbacks are still not solved, such as the difficulties that some procedures involve and/or the denaturalization of the protein due to the immobilization process. However, along with the chemical signals, the mechanical forces are critical for many tissues, since they are constantly suffering tension, shear, loading, etc. Essentially, the cell signaling exerted by forces is transduced through receptors that are in intimate contact with the matrix. Therefore, the main consequence of this receptor-matrix interaction is that cells and matrix are mechanically coupled, so that matrix deformation is considered the main cause of the mechanical signaling. By mimicking these mechanical forces in the surface of a material, it would be possible to obtain more physiological environments and thus a more physiological cell response. Again, the use of plasma polymerization techniques can help to design surfaces that can be tailored in terms of mechanical properties and chemical compositions and thus have a high potential for cells signaling.

This paper reports the work that we have developed in the last 10 years in the design, synthesis and characterization of thin films that can be a platform for studying the interaction between cells and separate influences of physical and chemical cues of a matrix on the adhesion, growth and final phenotype of cells.

11:40am **SM+AS+BI+PS-ThM12 Analysis of Amino Group Formation on Polystyrene Surfaces by Nitrogen-Hydrogen-Based Plasma Irradiation**, ***Kensaku Goto***, *D. Itsuki, M. Isobe, S. Sugimoto, S. Miyamoto, A. Myoui, H. Yoshikwa, S. Hamaguchi*, Osaka University, Japan

Polystyrene is a widely used cell-culture plate material. Currently cell culture plates on the market include those whose inner surfaces are covered with amino and/or carbonyl groups for a better control of cell adhesion to the plate surfaces. Such functional groups on a cell culture plate surface may immobilize glycoproteins or other biopolymers that function as extracellular matrices (ECM) and thus affect the environments where the cells are cultured. The goal of this research is to understand how such functional groups, especially amino groups, are formed on a polystyrene surface, depending on the deposition methods. Of particular interest are plasma-based methods of surface functionalization. In this study, we have observed experimentally how exposure of N_2/H_2 or N_2/CH_3OH plasmas to polystyrene surfaces form amino-group-like structures and also examined using molecular dynamics (MD) simulation how a polystyrene surface interacts with incident energetic ions such as NH_3^+ as well as abundant low-energy radicals such as NH_2 under conditions similar to our experiments. In the experiments, we used parallel-plate discharges with an inverter power supply whose peak-to-peak voltage was about 3kV and frequency was 20kHz at a relatively high gas pressure of 250 - 2,500 Pa. In MD simulation, we used a simulation code with interatomic potential functions that had been developed in-house based on quantum mechanical calculations of atomic interactions involved in this system. Results of MD simulations under the conditions similar to plasma enhanced chemical vapor deposition (PE-CVD) by ammonia plasmas or cyclopropylamine (CPA) [1] suggest that, with energetic ion bombardment, amino groups tend to be broken to form new covalent bonds by ion bombardment. Preliminary results of cell culture experiments with plasma-treated polystyrene cell plates will be also reported.

[1] A. Manakhov, L. Zajickova, *et al*. Plasma Process. Polym.11, (2014) 532.

12:00pm **SM+AS+BI+PS-ThM13 Tailoring the Surface Properties of Three-Dimensional, Porous Polymeric Constructs for Biomedical Applications Using Plasma Processing**, ***Morgan Hawker***, *A. Pegalajar-Jurado, E.R. Fisher*, Colorado State University

Utilizing bioresorbable polymers to fabricate constructs with three-dimensional (3D), porous architectures is desirable as these constructs mimic the extracellular matrix– a critical characteristic for many biomedical applications including tissue engineering, controlled-release drug delivery, and wound healing. Although the bioresorbability and architecture of these materials are suitable for such applications, the surface properties (i.e., chemical functionality and wettability) must often be customized depending on the desired function. Plasma processing is an attractive tool for surface modification of these delicate polymeric materials as it provides a low-temperature, sterile environment with a variety of precursor choices. The presented work will highlight the plasma modification of a variety of 3D, porous polymeric constructs. Specifically, we fabricated scaffolds via electrospinning and porogen leaching techniques using both poly(ε-caprolactone) (PCL) and polylactic acid (PLA) to develop a repertoire of native polymer constructs with differing bulk properties. We evaluated the efficacy of plasma-modifying 3D constructs using contact angle goniometry, X-ray photoelectron spectroscopy, and scanning electron microscopy to assess changes in wettability, chemical functionality, and scaffold architecture. The interactions of plasma-modified scaffolds with different biological species, including human dermal fibroblasts and *Escherichia coli* were explored, specifically to assess scaffold bioreactivity. Notably, we demonstrate that scaffold properties, and thus bioreactivity, can be customized depending on the choice of plasma precursor. We show that plasma treatment using fluorocarbon and hydrocarbon precursors (i.e., octofluoropropane, hexafluoropropylene oxide, and 1,7-octadiene) results in hydrophobic and bio-non reactive scaffolds. Additionally, precursors with nitrogen and oxygen functionality (i.e., allylamine, allyl alcohol, water, and ammonia) can be used to fabricate scaffolds that are hydrophilic and bio-reactive. Altogether, this work illustrates the comprehensive tunability of biologically-relevant polymeric constructs in terms of their bulk properties, surface properties, and cell-surface interactions.

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.

Surface Science
Room: 113 - Session SS+AS+EM+EN-ThM

Semiconductor Surfaces and Interfaces - I
Moderator: Yves J. Chabal, University of Texas at Dallas

8:00am **SS+AS+EM+EN-ThM1 Reaction of 1,2,3-Benzenetriol with the Ge(100)-2x1 Surface**, ***Tania Sandoval***, *S.F. Bent*, Stanford University

Functionalization of semiconductor surfaces can provide tunable control of interfacial properties in organic-inorganic hybrid devices. In particular, multifunctional molecules have the potential to change the surface chemistry by leaving unreacted functional groups available after adsorption. Understanding the adsorption of these complex molecules could lead to various applications as sensors, selective film deposition, and molecular electronics.

In this work, the reaction of 1,2,3-benzenetriol on Ge(100)-2x1 surface was investigated. While the reaction of hydroxyl groups has been previously studied, differences in selectivity can be expected due to the position of the functional groups along the ring. The purpose of this study is to determine the extent of these differences and the effect on product distribution.

An analysis of the adsorption energetics was carried out by density functional theory. As expected, a proton transfer reaction was shown to be the most stable adsorbate configuration. However, after the adsorbate reacts with the surface through its first OH group, the energetics of the second OH dissociation showed differences based on two factors: (i) surface configuration (cross or diagonal trench and end or cross bridge) and more interestingly (ii) which two of the OH groups (1 and 2 or 1 and 3) are reacting with Ge. The latter constraint affects the adsorption energy of the second dissociation, where adsorption regardless of the surface configuration is less stable when the OH groups are next to each other. Finally, transition states for dissociation of the third OH were found to be limited by the configuration of the second dissociation, and in some cases were not possible to find without unrealistic distortions of the molecule.

Chemisorbed and physisorbed O(1s) and C(1s) spectra were obtained by X-ray photoelectron spectra. Differences between these spectra can be used to identify the reaction products. No change in the C(1s) spectra was observed, suggesting that no carbon forms a bond directly with the Ge surface. On the other hand, clear differences between the chemisorbed and physisorbed O(1s) spectra are observed. The presence of a second peak with a lower binding energy only in the chemisorbed spectra, assigned to oxygen bonded to Ge, confirms that 1,2,3-benzenetriol reacts with the Ge surface through OH dissociation. Quantitative analysis of the chemisorbed O(1s) spectra provides information on the fraction of OH groups reacting with the surface. Interestingly, about 66% of the total hydroxyl groups in 1,2,3-benzenetriol are involved in reaction with Ge, indicating that there is a significant fraction of unreacted OH groups.

8:20am **SS+AS+EM+EN-ThM2 Ethylenediamine Grafting on Oxide-free H-, F-, and Cl- terminated Si(111) Surfaces**, ***Tatiana P. Chopra****, *R.C. Longo, K.J. Cho,* University of Texas at Dallas, *M.D. Halls,* Schrodinger, Inc., *P. Thissen,* Karlsruhe Institute of Technology, Germany, *Y.J. Chabal*, University of Texas at Dallas

Amine termination of surfaces constitutes a core platform for fields as diverse as microelectronics and bioengineering, and for nanotechnology in general. Diamines are particularly attractive for surface amination because, unlike ammonia or simple amine molecules, they have a metal chelating capability useful in fabricating heterostructures. They can act as a linker molecule between inorganic electronic materials and biomolecules or photoactive quantum dots for applications in microlectronic, photonics and biosensing. Most work in the field utilizes self-assembled monolayers (SAMs) on oxidized substrates to present an amine termination of the surface. However, grafting on oxides through silanes or phosphonates is not robust. Moreover, several applications require as short a distance between the substrate and the amine group, which is hindered by the thickness of the oxide. Therefore, diamine grafting directly on oxide-free substrates is important, yet remains unexplored.

In this work, the attachment of liquid and vapor-phase ethylenediamine on three types of oxide-free (H-, F- and Cl-terminated) Si(111) surfaces is examined by infrared absorption spectroscopy and X-ray photoelectron spectroscopy in conjunction with first-principles calculations. We find that chemisorption is only possible on F- and Cl-terminated Si surfaces, with H-terminated Si surfaces yielding only physisorbed diamine molecules. On Cl-terminated Si surfaces, diamines adsorb in a mixture of monodentate and bridging configurations (chemical reaction of both amine endgroups), while on partially F-terminated Si surfaces the adsorption occurs primarily at one end of the molecule. The reaction of ethylenediamine with Cl-terminated Si surfaces is also characterized by complete removal of Cl and partial Si-H (~25% ML) formation on the surface. This unexpected result suggests that a proton-chlorine exchange may take place, with the endothermic barrier possibly reduced via a silicon lattice assisted process after an initial attachment of ethylenediamine to the surface.

8:40am **SS+AS+EM+EN-ThM3 Reaction of Phenylhydrazine with Cl-Si(111) Surface by Wet Chemistry and with Clean Silicon Surface in UHV**, *A.V. Teplyakov*, ***Fei Gao***, University of Delaware

The monolayer coatings with aromatic functional groups can be used to tune mechanical, electronic, and chemical properties of semiconductor surfaces. This work focuses on obtaining well-defined surface of silicon functionalized with phenylhydrazine to produce an oxygen-free platform for further functionalization. Single crystalline Si(111) surface has been prepared using modified RCA procedure to produce well-ordered H-Si(111) surface. Next, Cl-terminated Si(111) surface is prepared from H-terminated Si(111) surface using PCl_5 in chlorobenzene solvent with trace amount of benzoyl peroxide as a reaction initiator under nitrogen atmosphere following previously established procedures. Phenylhydrazine-functionalized Si(111) sample is obtained from Cl-Si (111) surface with phenylhydrazine at 38^{o}C under N_2 atmosphere. To confirm the presence of Si-N bonds following this procedure, establish the structures of surface species produced and to investigate the oxidation mechanism, we followed the reaction by Fourier-transform infrared spectroscopy, X-ray photoelectron spectroscopy, and time-of-flight secondary ion mass spectrometry. To study the formation of Si-NH_x groups, this result was compared with the results of phenylhydrazine reactions on clean silicon surface under ultra-high vacuum (UHV) conditions. Density functional theory (DFT) calculations were performed to infer the mechanisms of surface reactions and further oxidation steps, and to compare the predicted vibrational spectra and core-level energies with the results of experimental studies.

9:00am **SS+AS+EM+EN-ThM4 Anomalously Low Surface Recombination Velocity for Fluorine Terminated Nanopatterned Si Surfaces**, *W.N. Peng,* ***Jonghan Park***, *L.-H. Liu, R.C. Longo,* University of Texas at Dallas, *D.J. Michalak,* Intel Corporation, *D.M. Pak, Y.J. Lee, J.X. Hsu, K.J. Cho, Y.J. Chabal*, University of Texas at Dallas

Recently, oxide-free and partially methoxy-terminated Si surfaces[1] have been developed as a novel platform for surface reactions because of their superior reactivity compared to hydrogen termination[2]. As a result, strong polar bonds such as Si-F could be stabilized on these surfaces. Since the electrical quality is critical for many applications (i.e. surface defects can degrade the device performance), we performed contactless surface recombination velocity measurements to examine the electronic quality of partially covered surfaces. Interestingly, we found that the carrier lifetime is significantly increased after fluorine termination, with the carrier lifetime 10 times higher than that of hydrogen terminated Si surfaces, approaching 1.5

*** Morton S. Traum Award Finalist**

ms. This anomalously long carrier lifetime can be explained either by a better surface passivation or by surface band bending effects. We therefore performed UPS and kelvin probe measurements to investigate the band structure of these surfaces after fluorine termination and found evidence for band bending. A potential model of a surface dipole layer induced band bending is supported by DFT calculations. Regardless of the mechanism controlling the recombination time, this method is well suited to explore the fluorination mechanism of H-terminated surfaces.

[1] D. Michalak, S. Amy, D. Aureau, M. Dai, A. Esteve, and Y. J. Chabal, *Nature Materials*, **9**, (2010)

[2] P. Thissen, T. Peixoto, R. Longo, W. Peng, W. Schmidt, K. Cho, and Y.J. Chabal, *JACS*, **134** (2012)

9:20am **SS+AS+EM+EN-ThM5 Molecular Functionalization of Semiconductor Surfaces: From Single Crystals to Quantum Dots**, ***Stacey Bent***, Stanford University **INVITED**

Because the surfaces of small structures can dominate their properties, implementing functional nanoscale materials depends to a large extent upon understanding and controlling the surface reactivity. This talk will focus on studies of the adsorption of organic molecules at semiconductor surfaces, toward the ultimate goal of controlling the chemical and electrical properties of the substrate. We will describe model studies of molecular functionalization on both flat and nanostructured surfaces. The presentation will begin by examining adsorption on the Ge(100)-2×1 surface. Using a combination of experimental (infrared spectroscopy, X-ray photoelectron spectroscopy) and theoretical (density functional theory calculation, Monte Carlo simulation) methods, we will show how the molecular structure as well as the identity of the reactive moieties of organic molecules can affect the product distribution upon adsorption. We will then present results of a study in which the organic ligands bonded to semiconductor quantum dots (QDs) are used to tune the electronic properties of the QDs. We will describe experimental and theoretical studies of the effects of such interface engineering on the band gap and relative band positions in lead sulfide (PbS) QDs. These ligand-exchanged quantum dots are tested in multilayer colloidal QD solar cells, and the results show that molecular functionalization can be used to achieve enhanced photogenerated carrier collection in the devices.

11:00am **SS+AS+EM+EN-ThM10 Periodic Trends in the Hydrogen Elimination Thermal Decomposition Reaction on Si(100)-2×1: Linear and Branched Alkyl Halides, Alcohols, and Amines**, ***Andrew Pohlman***, *K.L. Romolino, N.J. Burgener, S.M. Casey*, University of Nevada

The hydrogen elimination thermal decomposition reaction was studied on the Si(100)-2×1 surface using temperature programmed desorption mass spectrometry (TPDMS) and electronic structure methods for a selection of linear and branched alkyl halides, alcohols, and primary amines. Desorption activation energies and pre-exponential factors were determined using several analysis techniques from TPDMS spectra and compared to calculations based on ab initio canonical transition state theory using density functional theory (DFT). Values for activation energies and pre-exponential factors for dissociative desorption are compared within an adsorbate class based on a varying ratio of available alpha:beta:gamma hydrogens for elimination. Kinetic parameters are also compared between classes of adsorbates for general structure-activity periodic trends. TPDMS experiments reveal desorbing masses consistent with hydrogen elimination in all cases; however, the different elimination channels remain convoluted. Rate constants for each desorption channel were calculated using DFT and used to determine branching ratios for each dissociative desorption reaction. Reaction barrier trends are consistent with previous reports; however, numerical values were found to be much lower when considering inter-dimer reaction mechanisms.

11:20am **SS+AS+EM+EN-ThM11 Diffusion of Arsenic Oxides During the Atomic Layer Deposition of Metal Oxide Films on GaAs(100) Surfaces**, ***Alex Henegar***, *T. Gougousi*, University of Maryland, Baltimore County

It is known that native oxides of III-V semiconductors are consumed during atomic layer deposition using certain subsets of precursors. It was believed these surface oxides were completely removed during the first few deposition cycles because once the surface was covered by a coalesced film the native oxides would be protected. It has been observed, however, that native oxide consumption in systems such as ALD TiO_2 on GaAs(100) and InAs(100) proceeds continuously well after the surface is completely covered. Therefore there must be a transport mechanism that continuously moves these oxides through the developing film in order to interact with the precursor at the surface and be removed.

The aim of this work was to find unequivocal evidence of the transport mechanism needed for continuous oxide removal during ALD at typical processing conditions. ALD processes using metal organics and H_2O were used to deposit TiO_2, Al_2O_3 and HfO_2 films on GaAs(100). The experiments were designed so as to decouple the native oxide consumption from the native oxide transport and provide convincing evidence for the existence of this unacknowledged thus far mechanism. We will provide results that solidify the hypothesis that native oxide diffusion is a critical component in the complete and continuous removal of the interfacial layer.

11:40am **SS+AS+EM+EN-ThM12 Ultrafast Non-Equilibrium Effects in Ti Overlayers on P-Type GaAs(100) Investigated by Femtosecond XUV Photoemission Spectroscopy**, ***Mihai E. Vaida***, University of California, Berkeley, *S.R. Leone*, University of California, Berkeley and Lawrence Berkeley National Laboratory

Time resolution, surface sensitivity and element specificity are technical ingredients required to investigate ultrafast photoinduced processes and charge localization at semiconductor surfaces. All these requirements are fulfilled by a new experimental apparatus that consists of a tunable femtosecond high harmonics XUV source, a pump-probe setup, and an ultra-high vacuum surface science chamber for surface preparation and investigation.

The present contribution focuses on the charge carrier dynamics at the surface of a bare p-type GaAs(100) as well as Ti overlayers on p-type GaAs(100). The charge transfer between the bulk and the surface of the bare GaAs(100) is produced by the pump laser pulse at the central wavelength of 800 nm and is investigated by monitoring the surface photovoltage through the shift of the Ga 3d photoemission peak with the XUV probe laser pulse as a function of the pump-probe time delay. A transient shift of the Ga 3d photoemission peak to lower binding energy at early pump-probe time delay, with a magnitude of 0.3 eV, is observed and is attributed to transport of the electrons from the bulk to the surface. Upon increasing the pump-probe time delay, a restoration of the Ga 3d peak is observed, which corresponds to the recombination of the positive and negative carriers.

When a Ti overlayer is deposited on the p-type GaAs(100) surface, a Schottky diode is formed. If the 800 nm pump laser pulse has sufficient intensity to produce a photoemission process via multi-photon excitation, non-equilibrium effects occur at the Ti-GaAs interface independently from the presence of the surface photovoltage. In this case, positive charges accumulate at the surface and are not effectively screened by the electrons coming from the bulk, and the Schottky diode is transiently driven into a reversed bias mode. The formation of the reverse bias Schottky diode, which is studied in real time with the XUV probe laser pulse by monitoring the Ti Fermi level photoemission shift as a function of the pump-probe time delay will be presented and discussed.

12:00pm **SS+AS+EM+EN-ThM13 Improving the Quality of p-type AlGaN Layers by Reactive-ion Etching**, ***Joy McNamara***, *K.L. Phumisithikul, A.A. Baski, M.A. Reshchikov*, Virginia Commonwealth University, *J. Marini, F. Shahedipour-Sandvik*, SUNY Polytechnic Institute

AlGaN layers prepared by metal-organic chemical vapor deposition, with varying composition of Al (6 – 17%), were studied using the surface photovoltage (SPV) technique. Previous SPV studies on both *n* and *p*-type GaN allowed us to calculate the value of the surface band bending, by applying a thermionic model to explain the transfer of charges over the near surface barrier in various conditions (air, vacuum, and for a wide range of temperatures, T = 80 – 600 K). [1,2] The band bending was estimated to be 1.0 eV and – 2.0 eV, for *n*-type GaN and *p*-type GaN, respectively. SPV measurements on *p*-type AlGaN layers were expected to have similar behaviors to their *p*-type GaN counterparts. However, numerous measurements showed that this was not the case. The SPV transients (upon turning on or off the excitation source) showed significantly slower transients and smaller values than expected from the thermionic model. Moreover, the restoration of the band bending, as indicated by the restoration of the SPV signal to its dark value, did not occur within a reasonable amount of time. The data could not be fit by the thermionic model, and thus we were unable to calculate the band bending. We attribute the slow transients and lack of restoration to a defective surface region which interferes with thermionic processes. To verify this assumption, the top 40 nm of the AlGaN layer was etched using a reactive-ion etch (RIE). After etching, the SPV behavior exhibited substantially different behavior. Fast transients and close-to-thermionic behavior was recovered. Additionally, the effect of annealing the samples after etching provided even closer values to what is predicted by the thermionic model. From this study, it can be concluded that a defective, near surface region is inhibiting the transfer of holes over the near surface barrier under illumination, and hole trapping may be occurring during restoration. In both cases, this behavior cannot be modeled by theory. Etching removes the defective layer, and reveals a region of presumably higher quality as evidenced by the subsequent thermionic behavior.

[1] M. A. Reshchikov, M. Foussekis, and A. A. Baski. *J. Appl. Phys*. **107**, 113535 (2010).

[2] M. Foussekis, J. D. McNamara, A. A. Baski, and M. A. Reshchikov, *Appl. Phys. Let.***101**, 082104 (2012).

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 $3.5x10^{13}$ 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.

References:

[1] Nepal et al., Cryst. Growth and Des. **13**, 1485 (2013).

[2] Nepal et al., Appl. Phys. Lett. **103**, 082110 (2013).

[3] Kuo et al., Diamond & Related Materials **20**, 1188 (2011).

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 pinholes. 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 subsurface 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 subsurface 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$_x$Si 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$_x$Si) 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$_x$Si 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$_x$Si 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$_x$Si 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^{0}C) 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 $Pb(Zr_xTi_{1-x})O_3$ 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, ZrO_2, and TiO_2 layers using $Pb(TMHD)_2$, $Zr(TMHD)_4$, and $Ti(O^{\cdot}i\text{-}Pr)_2(TMHD)_2$ as metal precursors and H_2O 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^oC 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 ($(NtBu)_2(NMe_2)_2Mo$) 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 $(NtBu)_2(NMe_2)_2Mo$ 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 x 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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Tribology Focus Topic
Room: 230B - Session TR+TF-ThM

Nanolubricants and Coatings
Moderator: Tevis Jacobs, University of Pittsburgh

8:00am **TR+TF-ThM1 Mechanical Mixing and Wear Formation in Metallic Tribocouples**, ***Martin Dienwiebel***, *P. Stoyanov, T. Feser,* Karlsruhe Institut for Technology (KIT), Germany*, R. Merz,* Insitut für Oberflächen und Schichtanalytik GmbH, Germany*, P. Romero,* Fraunhofer Institute for Mechanics of Materials IWM, Germany*, F.C. Wählisch,* INM - Leibniz-Institute for New Materials, Germany*, P. Stemmer,* University of Duisburg-Essen, Germany*, M. Moseler,* Fraunhofer Institute for Mechanics of Materials IWM, Germany*, R. Bennewitz,* INM - Leibniz-Institute for New Materials, Germany*, A. Fischer*, University of Duisburg-Essen, Germany **INVITED**

During sliding of metallic surfaces in dry or lubricated conditions the near surfaces undergo significant changes in terms of topography, composition and microstructure [1] and a so-called *"third body"* or *"tribomaterial"* [2] develops. The third-body formation strongly influences the frictional and wear behavior of the system.

In this talk we present several experiments on pure metals and alloys that were performed using a novel experimental platform for the on-line correlation of friction, wear and topography under lubricated sliding [3]. Fast topography data is measured in real time by digital holography microscopy (DHM), wear is measured by the Radionuclide wear technique (RNT) and the nanoscale topography is obtained *in-situ* by liquid atomic force microscopy (AFM). The tribological systems that we recently studied include a-brass (CuZn) sliding against steel [4], tungsten and tungsten carbide [5], [6]. The experimental findings were compared to MD simulations. In order to characterize the mechanical behavior, nanoindentation and micropillar compression tests were performed that show that the third body material is softening during the initial running-in [7].

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8:40am **TR+TF-ThM3 Influence of MoDTC Degradation on Tribological Performances of Steel-Steel Contacts under Boundary Lubrication Conditions**, ***Clotilde Minfray***, *M. De Feo*, *M.I. De Barros Bouchet,* Ecole Centrale de Lyon - LTDS, France, *B. Thiebaut,* Solaize Research Center, France, *T. Le Mogne, B. Vacher, J.M. Martin*, Ecole Centrale de Lyon - LTDS, France

Nowadays, MoDTC is one of the best-known friction modifier additives used in engine oils for its friction reduction properties. A vast number of papers tackle the subject and converge on the fact that the generation of MoS_2 flake in the contact (in tribofilm) is at the origin of the friction reduction. But it is also known that this positive friction reduction effect is not so durable in time. Therefore, the investigation of MoDTC chemical degradation mechanism and its impact on the tribological properties in steel/steel contacts is of great interest.

It is proposed here to age a lubricant made of mineral base oil blended with 1%w of MoDTC with a thermo-oxidative procedure (open air - 160°C) for different durations. The aged lubricants are then tested under boundary lubrication conditions, with ball-on-flat reciprocating tests running at 100°C. Balls and flats are both in AISI52100 steel.

Concerning the results, clear differences are found in terms of friction behavior as a function of ageing time. A relation between ageing and induction time needed to reach the “low” friction regime is also established. Tribofilms generated on flats were then analyzed by means of XPS surface analysis and FIB-TEM observations for a precise chemical and morphological characterization of each flat sample. The possible presence of two types of molybdenum oxi-sulfide compounds, more or less oxidized, is suggested by XPS results and discussed regarding the friction behavior. Moreover, the TEM observations carried out suggest tribofilms differences in terms of morphology, size and organization. Finally, the effect of MoDTC ageing on friction behavior is discussed considering the composition of tribofilms but also taking into account MoDTC depletion in the bulk of the lubricant, thanks to High Performance Liquid Chromatography (HPLC) experiments.

9:20am **TR+TF-ThM5 General Model for Tribology of Metallic Contacts**, ***Michael Chandross***, Sandia National Laboratories, *S. Cheng,* Virginia Tech, *N. Argivay*, Sandia National Laboratories **INVITED**

The tribology community presently relies on phenomenological models to describe the various seemingly disjointed steady-state regimes of metal wear. Pure metals such as gold -- frequently used in electrical contacts -- exhibit high friction and wear. In contrast, nanocrystalline metals, such as hard gold, often show much lower friction and correspondingly low wear. The engineering community has generally used a phenomenological connection between hardness and friction/wear to explain this macroscale response, and thus to guide designs. We present a suite of recent simulations and experiments that demonstrate a general framework for connecting materials properties (i.e. microstructural evolution) to tribological response. We present evidence that the competition between grain refinement (from cold working), grain coarsening (from stress-induced grain growth), and wear (delamination and plowing) can be used to describe transient and steady state tribological behavior of metals, alloys and composites. We will present the results of large-scale molecular dynamics simulations and targeted experiments that explore the seemingly disjointed steady-state wear regimes of metals and alloys, with a goal of elucidating the structure-property relationships, allowing for the engineering of tribological mateirals and contacts based on the kinetics of grain boundary motion.

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11:20am **TR+TF-ThM11 Superlubric Sliding of Gold Nanoparticles on Graphite under Ambient Conditions**, *E. Cihan,* ***Mehmet Z. Baykara***, Bilkent University, Turkey

Forming a complete understanding of the physical mechanisms that govern friction on the nanometer and atomic scales is an ongoing endeavor for scientists from various disciplines. While atomic force microscopy (AFM) has proven to be invaluable for the detailed study of nano-scale frictional properties associated with various surfaces, issues related to the precise characterization of the contact formed by the probe tip and the sample surface remain largely unsolved.

In recent years, an alternative approach to nanotribology experiments has involved the lateral manipulation of well-characterized nanoparticles on sample surfaces via AFM and the measurement of associated frictional forces [1]. In line with this idea, we present ambient-condition nano-manipulation experiments involving gold nanoparticles (AuNP) thermally deposited on highly oriented pyrolytic graphite (HOPG), a sample system which has been recently characterized in detail [2]. It is observed that AuNPs experience remarkably low frictional forces during sliding. A detailed study of friction with respect to contact area firmly confirms the occurrence of *superlubric* sliding under ambient conditions for this sample system. The potential reasons behind the observed phenomenon are discussed with support from theoretical considerations.

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11:40am **TR+TF-ThM12 Monitoring the Gas-Phase Products of a Shear-Induced Reactions in Ultra-high Vacuum**, ***Heather Adams,*** University of Wisconsin-Milwaukee, *M.T. Garvey,* Illinois Applied Research Institute, *O. Furlong,* Universidad Nacional de San Luis, Argentina, *W.T. Tysoe*, University of Wisconsin-Milwaukee

Although tribochemical reactions are common in manufacturing, analysis of the mechanism and products is severely limited by the difficulty of probing a solid-solid interface that changes on small time scales. A method to analyze the gas-phase products of a tribochemical reaction in ultra-high vacuum has been developed to allow insight to be obtained into the decomposition pathways of short-chain alkylthiols on copper foils. A UHV-tribometer is used to probe the alkylthiol-covered copper foil by using a mass spectrometer to measure the products evolved from the surface.

Alkylthiols have been chosen due to their thermal stability on a copper surface[1], and their ability to form a tribofilm. Previous studies have found that sulfur moves into the sub-surface layer with rubbing, and the carbon is removed from the surface.[2]

The shear-induced decomposition of methyl thiolate produces gas-phase methane and measuring the amount of methane produced during each sliding cycle allows the shear-induced reaction rate to be measured. The results are analyzed to give insight into how sheer stress lowers the energy barrier for the decomposition reaction. [3]

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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.

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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.

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

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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.

Additive Manufacturing/3D Printing Focus Topic
Room: 211A - Session AM+EM+MS+TF-ThA

Additive Fabrication for Electronic Devices and Systems
Moderator: Jim Fitz-Gerald, University of Virginia, Gregory Whiting, Palo Alto Research Center

2:20pm **AM+EM+MS+TF-ThA1 Additive Printing for Flexible Electronic Devices**, *A.C. Pierre*, ***Ana Claudia Arias***, University of California at Berkeley **INVITED**

The area of printed electronics has been focused on the use of new classes of semiconducting and conducting materials in two main applications, displays and photovoltaics. Both applications require materials long-term stability, long shelf life as well the need for patterning and deposition over large areas. Over the past 10 years significant progress in the performance of printable materials has been reported including highly efficient solar cells, light emitting diodes and thin film transistors with mobilities as high as 10 cm^2/Vs. The work is highly motivated by the potential for high through put, high volume, low cost manufacturing. While large area electronics continues to be a good application for printed flexible devices, wearable medical devices, which benefit from new form factors, represent a good shift in direction of research in the field. Wearable medical sensors have the potential to play an essential role in the reduction of health care costs as they encourage healthy living by providing individuals feedback on personal vital signs and enable the facile implementation of both in-hospital and in-home professional health monitoring. In printed flexible electronics however, there are no standards for materials set, device models and fabrication methods. This lack of standards slows down design of new systems and the success of the technology as a whole. In this talk, I will review the state of the art of devices produced by printing and introduce a blade coating method that yields highly homogeneous flexible thin films that are applied to LEDS, photodiodes and TFTs. The application of these devices as building blocks for flexible electronics systems will also be discussed.

3:00pm **AM+EM+MS+TF-ThA3 Digital Microassembly for High-performance Printed Electronics**, ***Eugene Chow***, *J.P. Lu, G.L. Whiting, D.K. Biegelsen, S. Raychaudhuri, A.R. Völkel, J. Veres, P. Maeda, I. Matei, S. Nelaturi, L.S. Crawford*, Palo Alto Research Center (PARC) **INVITED**

Digitally printing micro-scale pre-fabricated building blocks instead of simpler materials enables an alternative route to printed electronics and opens up fundamentally new manufacturing capabilities. However, existing printing technologies do not provide the required accuracy and orientation control to print such micro objects. We will describe a demonstration of the fundamental process steps of such an electronic chip printer based on electrographic manipulation and xerographic concepts.

4:00pm **AM+EM+MS+TF-ThA6 3D Printed Bionic Nanomaterials**, ***Michael McAlpine***, University of Minnesota **INVITED**

The ability to three-dimensionally interweave biology with nanomaterials could enable the creation of bionic devices possessing unique geometries, properties, and functionalities. The development of methods for interfacing high performance devices with biology could yield breakthroughs in regenerative medicine, smart prosthetics, and human-machine interfaces. Yet, most high quality inorganic materials: 1) are two dimensional, 2) are hard and brittle, and 3) require high crystallization temperatures for maximally efficient performance. These properties render the corresponding devices incompatible with biology, which is: 1) three dimensional, 2) soft, flexible, and stretchable, and 3) temperature sensitive. These dichotomies are solved by: 1) using 3D scanning and printing for hierarchical, interwoven, multiscale material and device architectures, 2) using nanotechnology as an enabling route for overcoming mechanical discrepancies while revealing new effects due to size scaling, and 3) separating the materials synthesis and 3D printed assembly steps to enable conformal integration of high quality materials with biology. The coupling of 3D printing, novel nanomaterial properties, and 'living' platforms may enable next-generation nano-bio interfaces and 3D printed bionic nanodevices.

Applied Surface Science
Room: 212D - Session AS+SS-ThA

Advances in 2D Chemical Mapping and Data Analysis
Moderator: Kathryn Lloyd, DuPont Corporate Center for Analytical Sciences, Svitlana Pylypenko, Colorado School of Mines

2:20pm **AS+SS-ThA1 ASSD 30th Anniversary Lecture: Why Do (or Don't) People use Chemical State XPS Imaging?**, ***Julia Fulghum***, *K. Artyushkova,* University of New Mexico*, A. Barlow, P. Cumpson*, Newcastle University, UK **INVITED**

XPS imaging can be used to acquire chemical-state specific information with a spatial resolution of several microns. In response to perceived user interest, instrument manufacturers have put significant resources into developing chemical state XPS imaging and image processing capabilities. Current instrumentation allows for parallel image acquisition over a range of photoelectron energies, resulting in quantitative, lateral surface chemistry determinations. Although publications citing XPS continue to increase, XPS imaging contributes to only a small percentage of published work.

In this talk, we'll present an overview of laboratory XPS imaging capabilities using a variety of examples to demonstrate the practical (and not-so-practical) experiments that are possible. Recent multivariate and multitechnique analysis applications, including Multivariate Auger Feature Imaging (MAFI) and XPS-Raman image correlation will be used to highlight current research utilizing XPS imaging. Results from a survey of instrument manufacturers, directors of XPS user facilities, and expert users will be presented, including speculation as to why the use of XPS imaging has not met expectations, recommendations for using XPS imaging and hopes for future developments.

3:00pm **AS+SS-ThA3 X-ray Photoelectron Spectromicroscopy: Combining Spectral and Spatial Information for Materials Characterization**, ***Adam Roberts***, Kratos Analytical Limited, UK, *N. Fairley,* Casa Softaware Ltd, UK, *J.R. Mora*, University of Durham, UK

X-ray photoelectron spectroscopy is widely used in determining surface chemistry of materials. Improvements in instrument sensitivity mean that spectra are routinely acquired from areas with diameters in the tens of microns, although most routine analysis is performed at much larger areas. The assumption is that the material and spectra are homogeneous over the area probed is often made although it may not be true. Information of the lateral distribution of elemental and chemical states on a surface can be probed using XPS imaging either at a single binding (kinetic) energy or over a narrow energy range corresponding to a core-level photoemission peak.

Multispectral XPS imaging, also referred to as spectromicroscopy, where a series of images incremented in energy such that each pixel contains a spectrum, is relatively new and under exploited for surface characterisation. An advantage of spectromicroscopy is that spectral information can be reconstructed from defined areas which are smaller than those possible with focused x-ray or virtual probe selected area XPS. This means that the reconstructed spectra are no longer averaged over the total area from which the image is acquired such that both sample and instrument dependent differences can be studied.

The 256 x 256 pixel multi-spectral image contains >65,500 spectra which is ideally suited to multivariate analysis. Development of data processing to support spectromicroscopy data reduction has been necessary and a number of approaches have been successfully applied in the characterisation of model and real-world samples[1-3]. Multivariate analysis can be used to classify regions of interest across the field of view and data can be partitioned such that chemical state, changes in peak position and background shape can be investigated. Here we detail the use of spectromicroscopy for the characterisation of complex materials including functionalised multiwall carbon nanotubes (MWCNT). This approach has allowed the considerable challenges of surface analysis of such materials to be addressed and has allowed the influence of signal from the substrate material to be removed from the MWCNT of interest.

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3:20pm **AS+SS-ThA4 Optimizing XPS Imaging Acquisition**, ***Jon Treacy***, *C. Deeks, P. Mack, T.S. Nunney*, Thermo Fisher Scientific, UK

Surface structure and chemistry are properties that are crucial to the successful production and operation of numerous devices, materials and coatings. X-ray photoelectron spectroscopy (XPS) is an ideal tool for investigating these properties due to its inherent surface sensitivity, and ability to quantify the chemical states detected.

Whilst XPS is most often used for point analysis and/or depth profiling, it is also able to produce compositional maps of multi-phase materials. This is of particular use in scenarios where other surface science techniques are unsuitable, for example especially rough surfaces that cannot be imaged using SPM or surfaces with multiple phases of similar elemental composition, which cannot be differentiated by SEM-EDS. However the widespread implementation of XPS as a mapping tool has been hindered by the long acquisition times required.

Here we shall present the effects of increased x-ray performance, increased spectrometer sensitivity and modifications in data processing, i.e. both instrumental and software improvements, on the required acquisition time for XPS mapping. This is demonstrated using data from several samples, where multi-phase maps were acquired up to an order of magnitude more quickly than previously possible through implementation of these improvements.

4:00pm **AS+SS-ThA6 Enhancing Chemical Contrast: Latest Trends in Hyperspectral Image Analysis**, ***Barry Wise***, *W. Windig*, Eigenvector Research, Inc. **INVITED**

Many analytical techniques that were originally developed as single sample methods have been adapted to produce multivariate aka hyperspectral images where each pixel contains an entire spectrum. These imaging techniques are used to produce "chemical maps" which elucidate the arrangement and chemical makeup of areas on the surface. Imaging techniques produce an avalanche of data which is often underutilized. Multivariate statistical methods are increasingly being used to capture the information in these large data sets, condense it down to a manageable level, and improve the signal to noise ratio. This serves to enhance the chemical contrast in the images. This talk surveys methods for hyperspectral image analysis, discusses their pros and cons, and gives some examples demonstrating what can be accomplished. Methods considered include Principal Components Analysis (PCA), Multivariate Curve Resolution (MCR) with contrast constraints, Independent Components Analysis (ICA), Maximal Autocorrelation Factors (MAF) and sample clustering techniques.

4:40pm **AS+SS-ThA8 Unambiguous Molecular Identification with TOF-SIMS Imaging MS/MS**, *G.L. Fisher, J.S. Hammond,* Physical Electronics USA, *R.M.A. Heeren,* Maastricht University, The Netherlands, ***Scott Bryan***, Physical Electronics USA

First results from a new tandem imaging mass spectrometer will be presented. The unique TOF-TOF design allows the simultaneous collection of standard TOF-SIMS spectra *and* collision induced dissociation (CID) spectra of specifically selected precursors [1]. This new analytical capability maximizes the information content from a single acquisition and provides all data from the same analytical volume. The ability to acquire MS/MS data at the same primary ion beam repetition rate as used in conventional TOF-SIMS allows high speed image acquisition. The ability to unambiguously identify and image peaks above *m/z* 200 was applied to polymer additives and to the study of lipid composition changes in mouse spleen specimens infected with *F. novicida*.

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5:00pm **AS+SS-ThA9 Utilizing Chemical State Mapping to Reveal Spatially Distributed Dynamics in Model Nanostructured Battery Electrodes**, ***Alexander Pearse****, *E. Gillette, S.B. Lee, G.W. Rubloff*, University of Maryland, College Park

The rate at which a battery can deliver energy is ultimately dominated by the ability or inability to effectively transport both ions and electrons throughout the electrodes. When charge transport is a limiting factor, material utilization within the battery becomes spatially inhomogeneous, reducing performance. Additionally, the material and architectural requirements for optimizing transport for both ions and electrons are not always synergistic, which can lead to design challenges. The effects of architecture on device performance are generally characterized by externally measured scalar quantities, such as cell potential or current, but these quantities do not reveal where within the electrode any problem may lie. There is a growing need to develop models which can accurately predict spatially resolved dynamics within battery electrodes, as well as experimental techniques to verify them, particularly as nanoscience produces more and more sophisticated electrode designs.

Here we show that chemical state mapping with X-ray photoelectron spectroscopy (XPS) is a powerful tool for revealing transport-limit-induced dynamics within battery electrodes, and connect surface science with electrochemical modeling. We examine the specific problem of facile ion transport but limited electronic transport, which often occurs in high aspect ratio electrodes made of low conductivity semiconductors or insulators. While characterizing complex structures using XPS is normally very challenging, it is possible to gain much more useful and accurate information when a model device is designed from the ground up to exploit the strengths of XPS. By fabricating battery chips in which the anticipated gradients of material utilization (i.e. the spatially varying amount of lithium intercalated) are laid out laterally on a flat substrate, we can clearly map chemical changes in the electrode as a function of distance from a current collector. By using transition metal oxide (M_xO_y) cathode materials, we are able to track the state of charge through local quantification of the reaction $M^{n+} + e^- \text{->} M^{(n-1)+}$. Our data clearly reveal that as the applied current density increases, ion insertion activity is dramatically contracted towards the current collector, which leads to performance limitations at high rates. Importantly, we also use our spatially resolved data to validate the predictions of a sophisticated finite element multiphysics battery model. The visualization and understanding of design induced performance limits, as well as the validation of a predictive model, allow us to optimize the design of future high performance nanostructured battery electrodes.

5:20pm **AS+SS-ThA10 Microstructural and Chemical Mapping of Discharged Hybrid CF$_x$–SVO Cathodes from Primary Li Batteries**, *D. Reifsnyder Hickey*, University of Minnesota, ***Jeffrey Fenton***, *K. Chen, P. Yurek, J. Lesser, G. Jain*, Medtronic plc

Primary lithium batteries with hybrid carbon monofluoride–silver vanadium oxide (CFx–SVO) cathodes have become widely commercialized as power sources in implantable medical devices. Although CFx and SVO have been used separately as cathode materials, CFx–SVO hybrid cathodes have been developed to meet the increased energy-density, power, and longevity requirements specific to multiyear operation at physiological temperature. However, the microstructural basis for the performance characteristics has not been well understood, including chemical changes in the cathode materials as they discharge. This work presents a microstructural study of discharged cathode materials, aimed at identifying chemical and structural characteristics that can be related to the observed battery-performance characteristics. As a result, the relationships established can be used to improve the performance of future medical device technologies. Scanning electron microscopy with energy dispersive spectroscopy, X-ray photoelectron spectroscopy, and X-ray diffraction were used to probe the cathodes chemistry and structure. Although a single analytical method cannot give a full picture of the cathode chemistry and microstructure, the combination of these complementary techniques makes it possible to develop a clearer picture of the structural and chemical changes that occur within the cathode as the battery discharges. The discharged cathodes of SVO, CFx, and SVO-CFx hybrid are compared, which demonstrates that the relatively gradual transformation of SVO that occurs in SVO-only cathodes is accelerated in the hybrid cathodes. Several trends will be shown including: (1) SVO loses its crystalline structure and silver content (replaced by lithium) with discharge; (2) CFx converts into carbon and LiF with discharge; (3) and the hybrid cathodes show steady conversion of CFx, accelerated conversion of SVO (as soon as 5% depth of dischage), and the beginning of LiF formation (as early as 10% depth of discharge).

5:40pm **AS+SS-ThA11 A Novel Test Sample for the Spatially Resolved Quantification of Illicit Drugs on Fingerprints using Imaging Mass Spectrometry**, ***Shin Muramoto***, *T.P. Forbes*, NIST, *A.C. van Asten*, Netherlands Forensic Institute, *G. Gillen*, NIST

A novel test sample for the spatially resolved quantification of illicit drugs on the surface of a fingerprint using time-of-flight secondary ion mass spectrometry (ToF-SIMS) and desorption electrospray ionization mass spectrometry (DESI-MS) was demonstrated. Calibration curves relating the signal intensity to the amount of drug deposited on the surface was generated from inkjet-printed arrays of cocaine, methamphetamine, and heroin with a deposited-mass ranging nominally from 10 pg to 50 ng per spot. These curves were used to construct concentration maps that visualized the spatial distribution of the drugs on top of a fingerprint, as well as being able to quantify the amount of drugs in a given area within the map. For the drugs on the fingerprint on silicon, ToF-SIMS showed great success as it was able to generate concentration maps of all three drugs. On the fingerprint on paper, only the concentration map of cocaine could be constructed using ToF-SIMS and DESI-MS as the signals of methamphetamine and heroin were completely suppressed by matrix and substrate effects. Spatially resolved quantification of illicit drugs using imaging mass spectrometry is possible, but the choice of substrates could significantly affect the results.

Spectroscopic Ellipsometry Focus Topic
Room: 112 - Session EL+AS+BI+EM-ThA

Optical Characterization of Nanostructures and Metamaterials

Moderator: Bernard Drevillon, LPICM-CNRS, Ecole Polytechnique, France, Mathias Schubert, University of Nebraska - Lincoln

2:20pm **EL+AS+BI+EM-ThA1 Electrostatic Coating with Ligandless Copper Nanoparticles**, ***Lance Hubbard***, *A.J. Muscat*, University of Arizona

Electroless deposition (ELD) produces conformal coatings at low temperatures. ELD occurs by chemical reduction of metal ions without an externally applied potential or catalyst layer. In this paper, we report on a nonaqueous ELD process that uses a charge compensator, but not a ligand or complexing agent. The weak electrostatic attachment of the charge compensator to the ions and particles in solution and the high pH conditions improve the driving force for metal deposition. Si(100) native oxide was hydroxylated and terminated with a self-assembled amine layer (4 mM (3-aminopropyl)-trimethoxysilane in methanol). Metal films were deposited by suspending samples in a bath made by dissolving Cu(II) chloride in ethylene glycol (reducing agent), and adding 1-butyl-3-methylimidazolium tetrafluoroborate as a charge compensator. The Cu particle ion shell is attracted to the positively charged amine groups at high pH depositing a thin metal film that is both continuous and cohesive. Annealing the coupons at 200^{o}C in nitrogen promoted electrically conductive film formation. Electron microscopy images of the coated substrates showed a 80-95 nm thick film of 3 nm diameter particles. Four-point probe measurements of the films yielded electrical conductivities in the range 10^6-10^7 S/m (10-80% of bulk conductivty). The surface plasmon resonance (SPR) peak of the Cu nanoparticles in the bath and film was at 585 nm. Light scattering measurements and transmission electron microscopy (TEM) images yielded a size distribution of 3.1±1.56 nm. Scanning electron microsopy (SEM) images at various angles in relation to the films were taken to examine film morphology and thickness. Spectroscopic ellipsometry (SE) data were modelled with bulk, nanophase d-band transition, and SPR absorbances. The SE agreed well with UV-VIS results for the SPR and shows an increasing contribution from d-band transitions with increasing ionic liquid concentration. SEM and Fourier transform infrared (FTIR) spectroscopy were used to determine film thicknesses and chemistry.

2:40pm **EL+AS+BI+EM-ThA2 Using Plasmonic Effects to Design Ellipsometric Targets with Sub-Angstrom Resolution**, ***Samuel O'Mullane***, SUNY Polytechnic Institute, *J. Race, N. Keller,* Nanometrics, *A.C. Diebold*, SUNY Polytechnic Institute

For traditional ellipsometric targets, slightly changing the thickness of a layer or the index of refraction of a material results in a similarly small change in the observed spectra. If structures are designed to allow for plasmonic coupling, a slight change in those same parameters results in wildly different spectra. Specifically, localized plasmonic resonances in metallic grating structures allow for extraordinary sensitivity to parameters such as CD, sidewall angle and pitch.

*** ASSD Student Award Finalist**

Existing metallic grating structures are arrays of long, thin lines of copper that can be described using one dimension. The typical resolution for ellipsometric CD measurements on these structures ranges from nanometers to Ångströms. Because there is no confining second dimension, localized plasmons cannot be produced.

In order to obtain sub-Ångström resolution, additional structural modifications are required. This is achieved by adding a second metallic grating perpendicular to the original grating forming a cross-grating structure. Note that the added pitch and linewidth are an order of magnitude larger than the original parameters. This results in fully localized plasmonic resonances so that parameter variation on the order of tens of picometers could be detected through ellipsometric measurements. Making use of conical diffraction further increases the sensitivity to structural changes due to increased anisotropy.

These conclusions are the result of rigorous coupled wave-analysis (RCWA) simulations which were confirmed via finite element method (FEM) simulations. With both RCWA and FEM agreement, experimental confirmation is expected.

3:00pm **EL+AS+BI+EM-ThA3 Enhanced Temperature Stability of Slanted Columnar Thin Films by ALD Overcoating**, ***Alyssa Mock**, D. Sekora, T. Hofmann, E. Schubert, M. Schubert*, University of Nebraska - Lincoln

The demand for thermally stable nanostructures continues to increase as nanotechnology becomes ever more prevalent in both commercial and research applications. The high surface area of nanostructured thin films is susceptible to degradation under extreme temperatures. Scanning electron microscopy (SEM) and Mueller Matrix Generalized Ellipsometry (MMGE) were used to observe optical and structural properties of a glancing angle deposited cobalt slanted columnar thin film (SCTF) over increased annealing temperature. We show that the use of atomic layer deposition (ALD) to conformally passivate the SCTF surface provides both physical scaffolding and thermal protection during the annealing process up to 475°C as no changes in the SEM or MMGE results were present.

3:20pm **EL+AS+BI+EM-ThA4 Vector Magneto-Optical Generalized Ellipsometry on Heat Treated Sculptured Thin Films: A Study of the Effects of Al_2O_3 Passivation Coatings on Magneto-Optical Properties**, ***Chad Briley**, A. Mock,* University of Nebraska-Lincoln*, D. Schmidt,* National University of Singapore*, T. Hofmann, E. Schubert, M. Schubert*, University of Nebraska-Lincoln

We present the vector magneto-optical generalized ellipsometric (VMOGE) response[1] and model dielectric function (MDF) anisotropic hysteresis calculations[2] of ferromagnetic slanted columnar thin films under the effects of heat treatment up to 475° C. Directional hysteresis magnetization scans were performed with an octu-pole vector magnet at room temperature on Cobalt slanted columnar thin film samples grown by glancing angle deposition with and without Al_2O_3 conformal passivation overcoating done by atomic layer deposition. Analysis of the measured Mueller matrix ellipsometric data through a point-by-point best match model process determine the magneto-optical (MO) dielectric tensor. Three dimensional rendering of the anti-symmetric off-diagonal elements of the MO dielectric tensor displays anisotropic magnetic response of the thin film with the hard axis along the long axis of the columns. Data analysis reveals the preservation of anisotropic magneto-optical properties of the thin film with the passivated coating as compared to the non-passivated coating due to oxidation effects from heat treatment.

1) D. Schmidt, C. Briley, E. Schubert, and M. Schubert, Appl. Phys. Lett. **102**, 123109 (2013).

2) C. Briley, D. Schmidt, T. Hofmann, E. Schubert, and M. Schubert, Appl. Phys. Lett. **106**, 133104 (2015).

4:00pm **EL+AS+BI+EM-ThA6 Spectroscopic Ellipsometry for Critical Dimensions Analysis**, ***Vimal Kamineni***, GLOBALFOUNDRIES*, D. Dixit, S. O'Mullane,* SUNY Polytechnic Institute*, G. Iddawela, A. Vaid,* GLOBALFOUNDRIES*, A.C. Diebold*, SUNY Polytechnic Institute **INVITED**

In this talk an overview of the current applications of spectroscopic ellipsometry (SE) towards measuring the shape of nanostructures will be presented. The transition of the semiconductor industry from planar to 3D transistors has expanded the applications of ellipsometry. Ellipsometry measurements on the periodic nanoscale structures enable a diffraction based measurement technique referred to as scatterometry. The critical dimensions can be extracted by means of a regression on the diffracted light using rigorous coupled wave analysis (RCWA). RCWA is a Fourier-space method used to generate the optical response by slicing the periodic structure of interest and matching the boundary conditions to compute EM modes. This method is inherently dependent on *a priori* knowledge of the dielectric function of the materials that construct the nanostructures as well as the shape of the nanostructure obtained from reference metrology. Furthermore, time-to-solution is one of the main drawbacks of developing scatterometry applications due to the dependency on developing a robust model and for validating the model with reference metrology measurement. To address these challenges new methods such as signal response metrology (SRM) encompassing machine-based statistical learning and virtual reference metrology have been proposed. [1,2] These methods will be reviewed along with their benefits and limitations when applied to advanced 3D transistor structures. In addition, application of Mueller matrix ellipsometry measurements on strained grating structures (SiGe/Si) and block copolymer structures to determine the impact of strain and defectivity (bridging defects, wiggles, LER, etc.) on anisotropy coefficients will be presented, respectively. [3,4] Additionally, hybrid approaches will be proposed in conjunction with complementary/supplementary metrology methods (CD-SEM, HRXRD and CD-SAXS). [5-7]

[1] S. Pandev et al., SPIE Proc. 9424 (2015).

[2] A. Vaid et al., SPIE Proc. 9424 (2015).

[3] G. R. Muthinti et al., SPIE Proc. 8681 (2013).

[4] D. J. Dixit et al., Journal of Micro/Nanolithography, MEMS, and MOEMS 14, 021102 (2015).

[5] A. Vaid et al., SPIE Proc. 8324 (2012).

[6] A. C. Diebold et al., Proceedings of SPIE 8681, 86810I (2013).

[7] Charles Settens et al., Journal of Micro/Nanolithography, MEMS, and MOEMS 13, 041408 (2014)

4:40pm **EL+AS+BI+EM-ThA8 Structural and Ellipsometric Analysis of the Topological Insulator Bi_2Se_3**, ***Avery Green***, SUNY Polytechnic Institute

Topological Insulator (TI) materials have been the subjects of increasing scientific interest in the last decade. Their spin-momentum locked Dirac cone surfaces and insulating bulks have resulted in new directions in physics research and new spintronic devices. Though these materials have been thoroughly described in theory, the experimental realization and measurement of these surface states has been problematic, due to various crystalline defects. Theory predicts that TI surface states are protected against local defects, but it is essential to study the effects of global perturbations caused by surface oxidation, stoichiometric aberrations, and significant structural defect densities. The aim of this study is to measure the time-dependent dielectric function of the Bi_2Se_3 surface and bulk in air, using a dual rotating compensator spectroscopic ellipsometer. These data are backed up with various metrological measurements (AFM, cross-sectional TEM, EDS) to confirm surface topology and oxide thickness. This analysis of optical properties and oxide formation will, in the future, be used to optimize the Bi_2Se_3 flake thickness identification process, and provide a control for further necessary structural analysis, as stated above.

5:00pm **EL+AS+BI+EM-ThA9 Visible Luminescence in the VLS Grown Self Ga Doped ZnS Nanostructures**, ***Arshad Bhatti**, H. Hussain, M.A. Johar, S. Rehman, M.A. Shehzad, M.A. Hafeez*, COMSATS Institute of Information Technology, Pakistan

ZnS is a wide band gap semiconductor and thus offers fascinating opportunities for tailoring and tuning its bandgap states for photonic devices in visible region of the spectra. Ga introduced a strong red luminescence in ZnS. VLS mechanism was employed to synthesize ZnS nanowires using Ga as a catalyst and dopant simultaneously. The thickness of Ga ultrathin film was varied from 0.5 nm to 5 nm to observe the effect of Ga droplet size on the formation, lifetime and activation energies of defect states in the band gap. It was expected that Ga^{3+} would replace Zn^{2+} sites and dope ZnS, in addition, an impurity phase of Ga_2S_3 was also observed, whose content showed strong dependence of Ga thickness. It also shrunk the crystallinity of ZnS due to varied size of Ga^{3+}(76 pm) ions replacing Zn^{2+} (88 pm), which was observed in the shifts of major XRD reflections of ZnS. Incorporation of Ga introduced strong impurity states in the band gap of ZnS. It also affected the intrinsic defect states of ZnS, namely Zn and S vacancies (Please refer to Figure 1, which also shows the de-convoluted band gap broad band). In the PL spectra, blue (440 nm), yellow (560 nm), orange (600 nm) and red (680 nm) bands were attributed to S vacancies, Ga related defects, donor-acceptor recombination and Ga_2S_3, respectively. Photoluminescence excitation spectroscopy revealed strong absorbance at corresponding energies. A strong correlation of these states was observed in the temperature dependent PL measurements due to presence in their presence in the vicinity as the activation energies of these states matched the energy differences of corresponding states. The conductivity measurements also complimented the optical results. Time resolved PL demonstrated the lifetime of these states was between 0.5 ns to 1.5 ns and had somewhat significant effect of dopant concentration. Finally, Ga doped ZnS showed extremely efficient IR sensitivity.

Figure 1: The room temperature PL spectra of Ga doped ZnS nanowires synthesized with varied thickness of Ga: (a) 0.5 nm, (b) 1.0 nm, (c) 3.0 nm, and (d) 5.0 nm. The broad band between 450 nm to 750 nm has been deconvoluted to show contribution of various defect states (as mentioned in the Figure). These states were identified from the PLE spectrum.

5:40pm **EL+AS+BI+EM-ThA11 Can Front-Surface Metal Mirrors Be Protected from Oxidation by Vacuum Applied Polymer Films?**, ***David Allred***, *R.S. Turley,* Brigham Young University, *R.T. Perkins*, Utah Valley University

We have used variable-angle, spectroscopic ellipsometry to monitor secular changes in multilayers consisting of chemically active thin films, such as aluminum, deposited on dielectric-coated silicon wafers and protected by various vacuum-applied barrier layers. Ultrathin barrier layers included polymers such as parylene and rarely, sputtered inorganic films, such as silicon. Applications include the measurements of the oxidation of evaporated aluminum for use as a mirror in the VUV (vacuum ultraviolet) and the determination of the optical constants of materials such as Y_2O_3 potentially useful in VUV and XUV (extreme ultraviolet) optics.

Electronic Materials and Processing
Room: 211C - Session EM+EN-ThA

Materials for Light Management

Moderator: Michael Filler, Georgia Institute of Technology, Sang M. Han, University of New Mexico

2:20pm **EM+EN-ThA1 III-V Nanowires for Photonics and Solar Energy Applications**, ***Anna Fontcuberta i Morral***, EPFL, Switzerland **INVITED**

Semiconductor nanowires are filamentary crystals with a tailored diameter between few to few hundred nanometer. Their special shape and dimensions render them especially interesting for photonic applications. In my talk I will discuss several photonic applications of nanowires. I will start by showing how to modify light absorption and emission of nanowires by coupling them to plasmonic elements [1]. I will then follow by explaining the use of III-V nanowires for solar cell applications. I will show how, by choosing the adequate diameter and length, it is possible to obtain absorption cross-sections much larger than the nanowire physical size. This concentration effect can be used to increase the efficiency of nanowire-based solar cells and to reduce considerably the use of materials [2].

References

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[2] P. Krogstrup et al, Nature Photon. 7, 306 (2013) ; M. Heiss et al, Nanotech. 25, 014015 (2014)

3:00pm **EM+EN-ThA3 Formation of Wurtzite Phase by Si Doping and its Effect on the Optical Properties of GaAs Nanowires grown on Si Substrates by a Catalyst-free MBE-VLS Technique**, ***Marina Nakano***, *K. Sugihara, D. Ohori, K. Sakai,* Univ. of Miyazaki, Japan, *H. Amano, Y. Honda,* Univ. of Nagoya, Japan, *T. Ikari, A. Fukuyama*, Univ. of Miyazaki, Japan

GaAs nanowires (NWs) are expected to applying to optoelectronic devices. However, material properties have not been understood yet due to a presence of impurity and defect level related to an involved catalyst which was inevitable for growing nanowires. Recently, we succeeded in fabricating the catalyst-free GaAs NWs on a (111) Si substrates using a combination of molecular beam epitaxy and vapor-liquid-solid method [1]. The NW had two kinds of crystalline phases, a zinc-blend (ZB) and a wurtzite (WZ) structures [2]. We found the amount of WZ phase increased with increasing the amount of Si-doping by using high-resolution X-ray diffraction and transmission electron microscope [3]. In this study, we investigate the electronic band structure of Si-doped GaAs NWs by using a photoreflectance (PR) and a photoluminescence (PL) techniques and discuss the effect of Si-doping on the optical properties.

Three kinds of samples with different Si cell temperatures at 1015, 1065, and 1150ºC were grown. The average diameter and length of NWs were 60 nm and 35 mm, respectively. The amount of Si doping was evaluated by a carrier concentration estimated from a Hall measurement. The lowest hole concentration was 5.5×10^{17} cm^{-3} for the sample grown at 1015 ºc and increased about an order by increasing the cell temperature. PR and the PL emission light were carried at 4 K.

The crystallographic investigations showed that the amount of secondary WZ phase increased with increasing the Si-doping. Three critical energies were observed at 1.51, 1.49 and 1.43 Ev in the PR. The first two signals were observed for all samples and attributed to band to band and band to Si acceptor transitions, respectively. Since the signal at 1.43 Ev appeared only in high Si-doping sample with high amount of WZ phases, this is due to the band to band transition at the interface between the two different crystalline phases. In the PL spectra, three other emission peaks were observed at 1.46, 1.42 and 1.37eV. The intensities of these peaks changed for the samples with different cell temperature, these may be due to impurity and defect levels in nanowires. Si dopant itself as well as different crystal structure affect the electron transition. Since the interface transition observed at 1.43 Ev becomes dominant, emissions through such impurities were hidden for the sample with highest Si-doping. Temperature dependences of the PR and PL spectra will be discussed for further understanding the effect of Si-doping.

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[2] D. Spirkoska et al., Phys. Rev. B 80, 245325 (2009).

[3] A. Suzuki et al., Jpn. J. Appl. Phys. 54, 035001 (2015).

3:20pm **EM+EN-ThA4 Nanowire Enabled 3-Dimensional Band Engineering for Efficient Next Generation Solar Cells**, ***Esther Alarcon Llado***, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, *O. Demichel,* Universite de Bourgogne, France, *A. Fonctuberta i Morral*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland

Next generation photovoltaics (PV) aim to achieve large currents at high voltage by new materials and device concepts that overcome the main efficiency losses in traditional solar cells. Intermediate band solar cells (IBSCs) are a class of next generation PV where multi-energy levels in the semiconductor enable the scavenging of low energy photons and converting them into high voltage electrons. IBSCs have only been recently proven with highly mismatched alloys, however with very little efficiencies. The main challenge is the short lifetime of electrons at intermediate band states.

In this regard, the nanowire (NW) geometry offers potential advantages in the solar energy conversion process. Due to their richness in structure and morphology combined with doping and bandgap engineering, NWs provide an opportunity for new charge separation mechanisms.

In this work we propose a new IB-based solar cell design that is advantageously benefited from nanostructuring. We propose the use of core-shell heterostructures in order to reduce the optical coupling between the different band states in a three-level IBSC. Taking advantage of the intrinsic anisotropy of the nanowire geometry, the fundamental idea here is that excitons are separated by the heterostructure along the radial direction, while carrier extraction is performed along the axial direction. As a result, mid-gap recombination rate is reduced by several orders of magnitude.

On the other hand, it is known that optical resonances in NWs result into light self-concentrating effects that allow high absorption with reduced material. What's more, light resonances in NWs leave a very specific spatial distribution of light inside the nanostructure. By tuning the geometrical parameters of the NW, one can guide light around different regions in the NW depending on the photon energy. A combination of both electrical and morphological engineering, can lead to high efficiency PV.

4:00pm **EM+EN-ThA6 Effect of Internal Electric Field on the Miniband formation of Multi Quantum Well Solar Cell Structures Investigated by a Photoreflectance and a Photothermal Spectroscopy**, ***Tsubasa Nakamura***, *K. Matsuochi, T. Murakami, H. Suzuki,* University of Miyazaki, Japan, *K. Toprasertpong, M. Sugiyama, Y. Nakano,* The University of Tokyo, Japan, *T. Ikari, A. Fukuyama*, University of Miyazaki, Japan

Insertion of a multiple quantum-well (MQW) structure into the absorbing layer of solar cells is promising for accomplishing higher conversion efficiency. Recently, a MQW with a very thin barrier structure has been proposed to enhance the conversion efficiency [1]. The coupling of the wave functions between adjacent quantum wells causes a mini-Brillouin zone along the growth direction, which results in the formation of miniband. We have discussed carrier escaping mechanism in MQW by using photoreflectance (PR) and photothermal spectroscopy (PPT) and found that internal electric field in the QW region might affect the recombination probability [2]. In this study, we investigate the effect of internal electric filed on the miniband width.

Three kinds of MQW samples were grown by a metal-organic vapor phase epitaxy technique. Two GaAs p-i-n solar cell structure samples with MQWs in the i-layer were prepared. The doping levels in the p- and n-type layer were changed and this induced the different strength of the electric field in the absorbing layer. Another sample had GaAs n-n structures without any electric field in the absorbing layer. The thicknesses of the well barrier were changed from 2 to 6 nm for discussing the detailed miniband formation. PR and PPT measurements were carried out at room temperature. The miniband width was estimated from the difference of the peak energies of the PR modulus spectra. The lower and higher energy peak correspond to the energies of bottom and top of the miniband, respectively. The PPT method is used to detect the heat generated by non-radiative recombination of photo generated carriers. The miniband width was also calculated from the Gaussian decomposition technique of the observed PPT spectra [3].

Decrease of the miniband width by increasing the barrier width was observed for all samples. This is coincide with the theoretical prediction. The miniband width for n-n structure is considered to be larger than that of p-i-n structure. Applied electric filled may reduce the wave function overlapping between the adjacent wells. The increase of the miniband width by the electric field for the p-i-n structure sample was observed. However, the increase of the miniband widths for n-n structure could not be confirmed from the PR spectra. Since the PPT measurement is more sensitive for estimating the band edge transition, effect of the electric field may be more clearly observed by comparing the PR and PL spectra.

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4:20pm **EM+EN-ThA7 Controlling Light Absorption with Nanophotonics**, ***Vivian Ferry***, University of Minnesota **INVITED**

Luminescent solar concentrators (LSCs) offer many advantages over traditional concentrator geometries. As opposed to concentrators that rely on tracking, LSCs operate under both direct and diffuse illumination and require the solar cell to only be efficient at a small range of wavelengths. In practice, most LSCs suffer losses from reabsorption of emitted light, non-unity quantum yields, and incomplete light guiding to the solar cell. Here we combine tunable lumophores based on quantum dot heterostructures with photonic designs to improve the concentration efficiency of LSCs and study light propagation within the device.

To achieve high concentration ratios it is critical to have high effective Stokes shifts, high quantum yields, and to reduce escape cone losses. We synthesized a series of core-shell nanocrystal lumophores that exhibit tunable emission. We show how the narrow emission bandwidth of these nanocrystals enables the use of a 1D photonic mirror on the top surface of the device, designed to admit incident sunlight and trap luminesced light from the nanocrystal. In combination, the concentration ratios from these devices exceed the performance of dyes with higher quantum yields but broader emission. Another approach to photonic LSCs is to restrict the angle of emission from the lumophores to promote coupling to the total internal reflection modes of the LSC. This talk will discuss designs for the latter approach and compare achievable concentration factors.

The second portion of the talk will discuss light management strategies for solid-state lighting, and the incorporation of plasmonic nanostructures to enhance light outcoupling from solid-state devices. This section of the talk will compare and contrast plasmonic structures for solar cells and solid-state lighting, and discuss ways that design rules should be adjusted for different materials systems.

5:20pm **EM+EN-ThA10 Symmetry-Breaking in Periodic Nanostructures for Enhanced Light Trapping in Organic Solar Cells**, ***Seok Jun Han***, *S. Ghosh, O.K. Abudayyeh, E.J. Martin, J.K. Grey, S.M. Han, S.E. Han*, University of New Mexico

In this study, we introduce a new light-trapping scheme for organic solar cells by systematically breaking the symmetry in periodic nanostructures on the bottom metal contact. To create symmetry-breaking metal nanostructures, we start by fabricating a mold from a crystalline silicon (c-Si) substrate. We intentionally misalign the etch mask with respect to [110] crystallographic orientation of the c-Si. Subsequently, silver is sputter-coated over the nanoscale recess created in the c-Si substrate to create the metal nanostructures, and an organic photoactive material, PCPDTBT, is spin-coated on the silver layer. The enhancement in light absorption is achieved at surface plasmon resonances at the polymer-metal interface. We demonstrate that surface plasmon band structure can be tailored by symmetry-breaking. In experiment, we increase the number of surface plasmon bands in the visible spectrum and locate the bands at the desired wavelengths by controlling the symmetry. In general, by patterning a flat film in symmetry-breaking structures, absorption is enhanced from 65% to 85% in a broad short wavelength spectrum. Moreover, the absorption spectrum is extended into long wavelengths by 20 nm. We expect that our low-cost, symmetry-breaking fabrication strategy would be scalable and lead to a manufacturable process for efficient light-trapping in organic photovoltaic devices.

5:40pm **EM+EN-ThA11 Symmetry-Breaking in Light-Trapping Nanostructures on Silicon**, ***Sang Eon Han***, *S.J. Han, S. Ghosh, T. Cai, B. Hoard, S.M. Han*, University of New Mexico

In thin-film photovoltaics, highly absorptive materials are conventionally used. However, these materials have achieved efficiencies that are not comparable to those of thick crystalline silicon (c-Si) photovoltaics and, in some cases, suffer from their toxicity and low supply. A viable solution to these problems would be to use c-Si for thin-film photovoltaics. However, thin c-Si films absorb sunlight weakly because of its indirect band gap and strong light-trapping should be provided to achieve high efficiency. For thin-film photovoltaics, nanoscale structures are typically involved for light trapping because the film thickness becomes comparable to the wavelength of sun light. While diverse nanostructures have been studied to break the light-trapping limit of geometric optics, known as the Lambertian limit, highly efficient nanostructures that can be easily manufactured have not been demonstrated. We have previously predicted that symmetry-breaking in light-trapping periodic nanostructures on thin films can approach the Lambertian limit very closely. Herein, we will present how the systematic symmetry-lowering increases light-trapping in c-Si thin-film photovoltaics. We will demonstrate the experimental realization of such low-symmetry structures using simple wet etching methods on c-Si(100) wafers without any off-cut, tilt angle. Further, we will discuss the optical characterization of our fabricated structures on thin c-Si films.

Electronic Materials and Processing
Room: 210E - Session EM+MS-ThA

III-N Nitrides II
Moderator: Nikolaus Dietz, Georgia State University

2:20pm **EM+MS-ThA1 Accelerating Adoption of Wide Band Gap Semiconductors though Manufacturing Innovation**, ***John Muth***, North Carolina State University **INVITED**

As part of the national strategy for the United States to compete in the increasingly competitive global marketplace, a National Network for Manufacturing Innovation (NNMI) is being implemented to create a competitive and sustainable research-to-manufacturing infrastructure for U.S. Industry, academia and government to solve industry relevant problems.

PowerAmerica a $146 million dollar investment by the Department of Energy, Industry and the State of North Carolina is the second NMNI to be announced and with its industry and academic partners has initiated 20 projects focused on manufacturing wide band gap semiconductor devices and demonstrating their advantages in power electronic applications.

The mission of PowerAmerica is to develop advanced manufacturing processes to enable cost competitive, large-scale production of wide bandgap semiconductor-based power electronics, which allow electronic systems to be smaller, faster and more efficient than power electronics made from silicon. Innovations in manufacturing, improvements in reliability and demonstrations of system level advantages are important aspects of PowerAmerica's strategy to accelerate the adoption of wide band gap semiconductors into power electronics.

The number of systems that use power electronics between generation and use is about 20% today and is expected to grow to about 80% by 2030 a wide variety of technologies will be disrupted by the system advantages offered by wide band gap semiconductors. These include electric vehicles, motor drives, data centers, smart grid, photovoltaic and other renewable energy systems as well as niche applications in consumer electronics. In addition to the technical work performed in PowerAmerica a significant effort is being put towards workforce development and education. These efforts will prepare industry to compete in and the next generation of engineers and workers to lead the world into a brighter, more energy efficient world.

3:00pm **EM+MS-ThA3 InGaN/GaN Nanostructures for Efficient Light Emission and White Light Emitting Diodes**, *Y. Nakajima*, ***P. Daniel Dapkus***, *Y. Lin*, University of Southern California **INVITED**

InGaN/GaN quantum well LEDs that form the basis for efficient solid state lighting exhibit properties that limit the ultimate efficiency that can be achieved for this application. Among these deleterious properties are a high current efficiency decrease not related to heating – efficiency droop – and reduced efficiency in the green and yellow regions of the spectrum. It has been speculated that one of the causes for the droop and the reduced efficiency of green and yellow emitting diodes is the presence of piezoelectric fields that result from the growth of these structures on the polar (0001) plane of GaN.

In this work we report investigations of the formation of GaN nanostructures that are defined by non-polar and semi-polar planes that act as templates upon which quantum well active regions are formed. Nanorods, nanosheets, and nanostripe pyramids are described that are predominantly defined by {1-100}, {11-20}, and semi-polar planes and act as templates for the growth of InGaN/GaN multiple quantum well active regions. We describe the properties of blue LEDs formed on these templates and compare them to devices made on planar (0001) substrates.

Efficient green emitting LEDs and monolithic white light emitting LEDs require the extension of the range of efficient light emission in the InGaN / GaN materials system. We demonstrate high efficiency green and yellow light emitting multiple quantum well (MQW) structures grown on GaN nanostripe templates. The nanostripe dimensions range from 100 nm to 300 nm and have separations that range from 300 nm to 1 micron. Such small lateral dimensions are chosen to promote the elimination of threading dislocations from the structures. Nanostripes with various nonpolar and semi polar surfaces are grown with selective area growth on patterned c-plane GaN where the mask openings are oriented between the [10-10] and [11-20] directions. With stripes are aligned along the [10-10] and [11-20] directions, the sidewalls can be controlled to be nearly vertical or inclined and intersecting. Both shapes were examined and MQWs were grown on these different stripes. Photoluminescence (PL) measurement shows that MQWs grown on stripes with (10-11) surfaces and triangular shape emit the longest peak wavelength and have the best surface stability. Efficient PL emission peak wavelengths as long as 570 nm are realized on the triangular stripes with (10-11) surfaces by optimizing the MQW growth conditions for long wavelength emission. LED structures that utilize MQWs grown on nanostripes with (10-11) surfaces were fabricated to further demonstrate the viability of the approach.

4:00pm **EM+MS-ThA6 Tuning Bandgap Through Cation Ordering in New PV Materials**

Steve Durbin, *R.A. Makin, N. Feldberg,* Western Michigan University*, J.P. Mathis, N. Senabulya, R. Clarke*, University of Michigan

There continues to be considerable interest in so-called earth abundant element compound semiconductors, of which we have multiple candidates at present. One material worth considering, ZnSnN$_2$, is properly termed a ternary heterovalent compound and is a member of the more general family of II-IV-V$_2$ semiconductors. It is analogous to InN, whereby pairs of indium atoms are replaced by a periodic arrangement of a Zn and Sn atom, and in that way is related to CIGS as that material corresponds to II-VI semiconductors. Although ZnSnN$_2$ is predicted to crystallize in an orthorhombic lattice with a bandgap of approximately 2.0 eV (calculations reported in the literature vary somewhat), we have observed that single crystal thin films grown by plasma-assisted molecular beam epitaxy are more likely to form in a wurtzitic lattice, with a lower electronic bandgap energy. In fact, we have recently observed both optical absorption and x-ray emission spectroscopy results on a series of films which agree with density functional theory calculations predicting a bandgap as small as 1 eV - the direct consequence of disorder in the cation sublattice. Careful tuning of the growth parameters enables the degree of order to be varied, and consequently the bandgap energy as well. This provides the intriguing possibility of tuning the bandgap through the growth process, as opposed to the traditional approach of alloying. The optimal bandgap energy of approximately 1.5 eV would therefore be an intermediate state between the two extremes.

4:20pm **EM+MS-ThA7 Comparison Studies of GaN Grown with Trimethylgallium and Triethylgallium for Optoelectronic Applications**

Mustafa Alevli, Marmara University, Turkey*, A. Haider,* Bilkent University, Turkey*, N. Gungor,* Marmara University, Turkey*, S. Kizir, S. Alkis, A.K. Okyay, N. Biyikli*, Bilkent University, Turkey

Si is famous for the well-developed mature CMOS technology and a promising substrate for GaN due to its wafer size, low material cost, and possible integration with the CMOS. However, it is very difficult to deposit high-quality GaN films on Si due to its high deposition temperature which results in inter-diffusion at the GaN/Si interface and the relatively large lattice mismatch. Atomic layer deposition is a low temperature technique that can provide an alternative path for the deposition of GaN on Si.

In this study, GaN materials were grown at 200°C by two different kinds of metalorganic precursors, one by using trimethylgallium (TMG) and another by using triethylgallium (TEG) as gallium sources. It is reported that the carbon concentration was fifty times higher in the GaN films grown by TMG precursor than in that grown by TEG precursor. As it is going to be shown in this contribution, optical and electrical properties of Hollow cathode plasma-assisted atomic layer deposition of crystalline GaN films will be presented. When TMG pyrolyzes, it introduces more reactive CH$_3$ radicals in to the CVD reactor when it is compared to TEG precursor. It means that TMG enhances carbon incorporation in epitaxial film structure. Spectroscopic ellipsometry studies on GaN films shows that refractive indices of GaN films increase when TMG was used as metalorganic precursor. The increase in the refractive index values indicates that the crystalline quality of GaN films improved with the use TMG. The change in the metalorganic precursor did not affect either the Bragg peak positions or crystalline phase of deposited GaN films. The grazing-incidence XRD patterns of both GaN films revealed that the films are polycrystalline with hexagonal wurtzite structure and are referring to (100), (101), (002), (102), (110), and (103) planes. The increase in the intensity and improvement in the FWHM value of the (002) peak also showed that the crystallinity improved for TMG grown GaN films. Further More,. The effect of alkyl precursors is also studied by a variety of characterization techniques Fourier Transform infrared reflectance, optical transmission, X-ray photoelectron spectroscopy, current-voltage characteristics of which the results will be discussed in detail.

This work is supported by TÜBİTAK project #114F002.

4:40pm **EM+MS-ThA8 Growth Control of InGaN Alloys and Nanostructures by Migration-Enhanced, Plasma-Assisted MOCVD**

Daniel Seidlitz*, I. Senevirathna, Y. Abate, N. Dietz,* Georgia State University*, A. Hoffmann*, Technical University Berlin, Germany

This contribution will present results of the structural and optoelectronic properties of InN and InGaN alloys and nanostructures as a function of temperature, reactor pressure and the temporal injection of metalorganic precursors and plasma activated nitrogen species (e.g. N*/NH*/NH$_x$*).

Migration-enhanced plasma-assisted metal organic chemical vapor deposition (MEPA-MOCVD) is utilized for the growth of InN and InGaN layers and nanocomposites at growth temperatures in the range of 450°C and 700°C. The custom-built MEPA-MOCVD system consists of a showerhead reactor combined with a hollow cathode (HC) plasma source (Meaglow) powered by a high-frequency (13.56 MHz) RF generator with a output power up to 600W. The HC plasma source creates reactive nitrogen fragments, which afterglow region approaches the growth surface. Plasma emission spectroscopy (PES) is utilized for real-time information about the formation and concentration of plasma generated active species. Added provisions allow a spatial and temporal injection of both, nitrogen and metalorganic precursors and enable the control of the epitaxial layers and their composition during the growth process.

Ex-situ investigations by Atomic Force Spectroscopy (AFM) as well as Fourier Transform Infrared Reflectance (FTIR) and Raman spectroscopy assess structural and optoelectronic properties (e.g. surface roughness, high-frequency dielectric constant e$_\infty$, film thickness, etc.) of the deposited InN and InGaN nanostructures.

Correlation of the in-situ obtained plasma characteristics with the ex-situ results of the structural and optical properties of the InN and InGaN nanostructures are provided, as well as correlations between plasma afterglow regime position above the growth surface and the epitaxial layer properties. The aim of these studies is to access the phase stability regime of indium-rich ternary group III-nitrides as a function of growth temperature, kinetic energy of plasma species, reactor pressure, and temporal and spatial precursor supply.

5:00pm **EM+MS-ThA9 GaN on Rare-earth Oxide Buffer –A New Player in GaN-on-Si Technology**

Rytis Dargis*, A. Clark*, Translucent Inc.

We present the results of process development for GaN MOCVD epitaxial growth on Si using single crystal rare-earth oxide buffer layers. Advantage of this technological approach over traditional GaN-on-Si that uses a AlN nucleation buffer is the chemical isolation of the Si substrate from the group-III metals thereby preventing Si diffusion into the III-N layer. This removes one of the main breakdown failure modes being the silicon doped interface. Additionally, the relatively high breakdown electric field of rare-earth oxides (e.g. 4MV/cm for erbium oxide) can be used as part of the overall vertical breakdown thereby reducing the thickness of the III-N layer structure without impairment of electrical breakdown properties of a power device. This is important to the overall process since thinner GaN not only reduces MOCVD cycle time but results in lower stress in the structure. Additionally, thermal and chemical stability of the oxides opens up opportunity for implementation of a more flexible process for GaN-on-silicon including solutions used in GaN-on-sapphire.

Two types of the oxide buffers with thickness of 300 nm were grown of Si (111): single Er$_2$O$_3$ and double layer Er$_2$O$_3$-Sc$_2$O$_3$ structure were employed. Robustness and scalability of the oxide process make it suitable for manufacturing.

To validate the technology, the standard AlN-first process was used. GaN with thickness of 2 µm was grown in a state of the art 200mm manufacturing tool. It demonstrated excellent management of the stress in the structure with 25µm convex curvature, superior surface morphology

(RMS = 0.56 nm, Z-range = 4.1 nm) and good crystal structure (GaN (002) FWHM = 561 arcsec, GaN (102) FWHM = 907 arcsec).

Our newly developed GaN-first MOCVD process, which is based on a typical GaN-on-sapphire process, uses nitridation and low temperature GaN buffer. During the growth, the upper part of the oxides is transformed into rare-earth nitride with lattice constant smaller than that of the oxide and consequently lower lattice mismatch to GaN (e.g. lattice constant mismatch between GaN and ScN is approximately -0.2%). The GaN layers with total thickness of 2.5 μm grown on the both types of the buffers exhibit smooth surface with RMS < 1 nm and Z-range <10 nm. The wafers exhibit good structural quality with X-ray diffraction GaN (002) peak FWHM of 540 arcsec and 684 arcsec for GaN on Er_2O_3 layer and Er_2O_3/Sc_2O_3 stack respectively. SIMS data shows no oxygen or rare-earth metal diffusion into the GaN.

5:20pm **EM+MS-ThA10 Plasma Enhanced Atomic Layer Deposition of Al_2O_3 on AlGaN/GaN High Electron Mobility Transistors**, ***Xiaoye Qin***, *R.M. Wallace*, University of Texas at Dallas

Metal insulator semiconductor AlGaN/GaN high electron mobility transistors (MISHEMTs) are promising for power device applications due to a lower leakage current than the conventional Schottky AlGaN/GaN HEMTs. Among a large number of insulator materials, Al_2O_3 dielectric layer, deposited by atomic layer deposition (ALD), is often employed as the gate insulator because of a large band gap (and the resultant high conduction band offset on AlGaN)[1], high breakdown field, conformal growth, and a relatively high dielectric constant. However, the thermal ALD Al_2O_3 does not passivate the surface effectively according to our previous work.[1–4] In this work, the half cycle study of plasma enhanced atomic layer deposited (PEALD) Al_2O_3 on AlGaN is investigated using *in situ* X-ray photoelectron spectroscopy (XPS), low energy ion scattering (LEIS) and *ex situ* electrical characterizations. A faster nucleation or growth is detected in PEALD than thermal ALD using an H_2O precursor. The PEALD Al_2O_3 layer decreases the gate leakage current as the ALD Al_2O_3. Importantly, the remote O_2 plasma oxidizes the AlGaN surface slightly at the initial stage, which passivates the surface and reduces the OFF-state leakage. This work demonstrates that PEALD is a useful strategy for Al_2O_3 growth on AlGaN/GaN devices.

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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 the 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.

Plasma Science and Technology
Room: 210B - Session PS+AP+SE-ThA

Advanced Ion Implantation and Plasma Doping
Moderator: Aseem K. Srivastava, Applied Materials, Inc.

2:20pm **PS+AP+SE-ThA1 Evolutionary Trends in Ion Implantation**, ***Anthony Renau***, Applied Materials, Varian Semiconductor Equipment **INVITED**

Since the 1960s and 1970s ion implantation has been used for the p- and n-type doping of semiconductors. The ability of ion implantation to abruptly alter the stoichiometry of the substrate has made it a very attractive technology for making transistors with the required drive characteristics, by accuratley manipulating dopant concentrations in the contact and channel regions. It is used to control carrier density, channel length, contact resistance, isolation and other key device attributes.

There have been significant enhancements to enable ion implant to continue to meet semiconductor doping needs. These include the development of ribbon ion beams, substrate temperature control, accurate beam angle control and novel methods for precisely varying the dose over the substrate. These improvements have also enabled the technology to be used for a rapidly growing number of non-doping applications.

Today, the majority of implants are done not for doping, but are instead used for some form of materials modification or engineering. These include, for example, strain control, pre- or post-treatments to improve some other process step, and lattice enginering for isolation or diffusion control.

In this paper we will discuss some of the improvements to the technology and the applications that have benifited from these. We will also describe how directed ribbon beam technology, similar to that used for implanters, can also be used to improve materials engineering applications as diverse as etch and CMP.

3:00pm **PS+AP+SE-ThA3 Conformal Arsenic Doping using a Radial Line Slot Antenna Microwave Plasma Source**, ***Hirokazu Ueda***, Tokyo Electron Limited, Japan, *P. Ventzek*, Tokyo Electron America, Inc., *M. Oka, Y. Kobayashi, Y. Sugimoto*, Tokyo Electron Ltd., *T. Nozawa*, Tokyo Electron Ltd., Japan, *S. Kawakami*, Tokyo Electron Ltd. **INVITED**

Doping and activation of non-planar topographic structures is important for the fabrication of functional FinFET and nanowire based devices to name a few. Conformal plasma arsenic doping of topographic (fin) structures was achieved using RLSA^{TM} microwave plasmas with low temperature annealing. To show that the arsenic concentrations were identical at the fin top and sides, dopant concentrations were measured precisely by TEM and SEM EDX for both plasma doping and subsequent annealing steps. We found that doping using plasmas generated by lower RF bias operation coincident with high microwave power was key to obtaining perfectly conformal arsenic dose/profiles after annealing. The RLSA^{TM} microwave plasma facilitates high enough electron density at the plasma generation region to supply enough reactive dopants for sufficient dose. The high plasma density plasma allows for operation in a low RF power and high process pressure regime. This regime yields ions with sufficient flux and energy for dopant integration into and redistribution around the topographic structure. At the same time low enough energy ions can be controllably accessed to ensure fin damage is eliminated. We also demonstrate optimized rf bias power of the microwave RLSA^{TM} plasma enables additional control of dopant conformality post SPM wet cleaning step. The wet clean poses a significant challenge for dose retention as cleans tend to remove oxidized or otherwise disordered silicon material. The source of dose retention is shown to be related to dopant transport through a ternary (As-Si-O) oxide layer, segregation effects and the stable nature of the oxide. The presentation will include experimental and computational results related to dose conformality and retention. Comments related to the future of plasma doping technology including advanced materials, metrology and control will round out the presentation.

4:00pm **PS+AP+SE-ThA6 Practical Application of Atom Probe to Analysis of Ion Implantation**, ***Ty Prosa***, CAMECA Instruments Inc. **INVITED**

Characterization of implanted dopants and impurity atoms within individual silicon nano-devices is critical to the semiconductor industry. While secondary ion mass spectrometry (SIMS) depth profiles achieve a high level of quantification with ion implanted standards in various matrices, atom probe tomography (APT) offers a unique combination of high analytical sensitivity coupled with high spatial resolution [1]. SIMS achieves its sensitivity by analyzing relatively unconstrained sample volumes, analyzed areas often greater than several hundred square microns. Square microns of material cannot be analyzed by APT and so it can never compete with SIMS for sensitivity at the micron scale; however, the situation is very different at the nanoscale—the regime of individual device volumes. Within this regime APT has high, uniform, quantitative chemical sensitivity with sub-nanometer spatial sensitivity.

Understanding the precision and accuracy of APT when applied to ion implanted dopant profiles is essential for general adoption by the semiconductor industry. Three-dimensional atom positions are determined using a simple point-projection methodology [2]. Adopting best practices within the constraints of this methodology is necessary to allow uniform and unbiased determination of atom positions and depth profiles. Although the ultimate sensitivity of APT is determined by counting statistics, it is well known that counting statistics alone do not fully account for accuracy limitations. The free parameters available within the reconstruction process are often dominant in terms of total observed error.

During this presentation, a number of examples will be shown of APT applied to the analysis of dopant distributions in relevant structures. The focus will be ion implanted structures with discussion of best practice approaches to minimize error and remove bias by the practitioner. Material structures include a series of NIST Standard Reference Material implants into silicon [3] and additional implants into GaN-based materials.

[1] T.F. Kelly and D.J. Larson, *Annual Reviews of Materials Research* 42 (2012) 1.

[2] P. Bas et al., *Surf. Sci.* 87/88 (1995) 298.

[3] R.R. Greenberg et al., *Radioanal. Nucl. Chem,* 245 (2000) 57.

4:40pm **PS+AP+SE-ThA8 Optical Emission Spectroscopy to Determine Plasma Parameters in an Oxygen Inductively Coupled Plasma**, ***Nathaniel Ly***, *J. Boffard, C.C. Lin, A.E. Wendt,* University of Wisconsin - Madison, *S. Radovanov, H. Persing, A. Likhanskii*, Applied Materials, Inc.

The success of ion implantation to precisely modify substrate properties requires control of the incident ion energies to achieve the desired depth of the implanted ions. Oxygen plasmas generally contain both O^+ and O_2^+ positive ions, and in plasma immersion ion implantation (PIII) of oxygen, the two will produce different concentration depth profiles due to their different energy/mass ratios. Predicting the overall profile thus requires knowledge of the relative fluxes of the two ion species. Motivated by the long term goal of a robust predictive model, here we combine experiment and numerical simulation to investigate the feasibility of using non-invasive optical emission spectroscopy (OES) to monitor plasma parameters in an oxygen inductively-coupled plasma. Initial experiments made use of a small admixture of argon with the oxygen to take advantage of established techniques involving argon OES. In addition to recording argon emissions, measurements of multiple O, O_2, O^+, and O_2^+ emission intensities were made as a function of pressure (1-30 mTorr) and power (500-2000 W). An emission model makes use of available electron impact excitation cross sections for argon and atomic and molecular oxygen to relate measured emission spectra to corresponding plasma parameters, including electron temperature and the dissociation fraction of the neutral oxygen. Data taken while as a function of the percentage of argon in the Ar/O_2 mixture showed that even a very small admixture of argon significantly affected the oxygen plasma properties, and more recent experiments have thus focused on oxygen OES in a pure oxygen plasma. The CRTRS 2D/3D plasma code self-consistently and semi-implicitly solves for ICP power deposition and uses Poisson's equation to solve for the electrostatic potential and dynamics of electrons and ions in the drift-diffusion approximation (or full momentum equations). The code also solves for the electron temperature, and generation and quenching of excited states as well as their dynamics. The experimental results are used in combination with simulation predictions to understand the dependence of plasma parameters, including the relative fluxes of O^+ and O_2^+, on the operating parameters.

The authors acknowledge support from NSF grant PHY-1068670.

5:00pm **PS+AP+SE-ThA9 Adhesion Improvement of Carbon Nitride Coatings on Steel Surfaces by Metal Ion Implantation using HiPIMS**, ***Konstantinos Bakoglidis***, *G. Greczynski, S. Schmidt, L. Hultman*, Linkoping University, Sweden

Carbon based thin films are materials with low friction and wear resistance. Deposition of C based thin films as coatings on steel substrates can enhance the tribological performance of steel surfaces. Adhesion of magnetron sputtered C based coatings on steel substrates is, however, often insufficient, leading to film delamination or flaking after the deposition. Adhesion is essential when such films are exploited in tribological applications and can be improved by using ion etching of the steel surface prior to film deposition. Several ion etching techniques are used, among them metal ion etching, for ion implantation in order to prepare the steel surface for the C film deposition. Moreover, high power impulse magnetron sputtering (HiPIMS) offers high metal ionization conditions and effectively enhances ion implantation into the steel subsurface. In this study, we used four different metal targets, namely Al, Cr, Zr, W, in HiPIMS mode in Ar-based plasma with a pressure of 200 mPa, and under a negative applied bias voltage of 900 V, which was synchronized with the cathode pulse. All targets were operated with an energy per pulse of 15 J, with pulse width of 200 μs, an etching time of 30 s, while the frequency was set at 100 Hz. A carbon nitride (CN_x) thin film was deposited after each etching step, using a graphite target in DC mode, operated at 1400 W, in a N_2/Ar gas mixture with a ratio of 0.16, and at a temperature of 150 °C, while the pressure was kept constant at 400 mPa. In all cases except Zr, a thin metal interlayer was obtained, with thicknesses < 20 nm, while adhesion of CN_x films on steel surface was dramatically improved when W ions were used for the pre-treatment phase.

Plasma Science and Technology
Room: 210A - Session PS-ThA

Plasma Sources
Moderator: Cheng-Che Hsu, National Taiwan University

2:20pm **PS-ThA1 Control of Electron Heating and Ion Energy Distributions in Capacitive Plasmas by Voltage Waveform Tailoring based on a Novel Power Supply and Impedance Matching**, ***Birk Berger***, *J. Franek, St. Brandt,* West Virginia University*, M. Liese, M. Barthel,* Barthel HF-Technik GmbH, Germany*, E. Schuengel, M. Koepke, J. Schulze*, West Virginia University

We present a novel radio-frequency (RF) power supply and impedance matching to drive technological plasmas with customized voltage waveforms. It is based on a system of phase-locked RF generators that output single frequency voltage waveforms corresponding to multiple consecutive harmonics of a fundamental frequency. These signals are matched individually and combined to drive an RF plasma. Electrical filters are used to prevent parasitic interactions between the matching branches. By adjusting the harmonics' phases and voltage amplitudes individually any voltage waveform can be realized as a customized finite Fourier series. This RF supply system is easily adaptable to any technological plasma for industrial applications and allows the commercial utilization of process optimization based on voltage waveform tailoring for the first time. Here, this system is tested on a capacitive discharge based on three consecutive harmonics of 13.56 MHz in Argon with an admixture of Neon as tracer gas for Phase Resolved Optical Emission Spectroscopy (PROES). Measurements were performed for gap lengths of 30mm and 40mm, different pressures (p=3, 5, 200Pa) and varying applied voltages (V=120, 210V). According to the Electrical Asymmetry Effect, tuning the phases between the applied harmonics results in an electrical control of the DC self-bias and the mean ion energy at almost constant ion flux. A comparison with the reference case of an electrically asymmetric dual-frequency discharge reveals that using more than two consecutive harmonics significantly enlarges the control range of the mean ion energy. Additionally, the effect of tuning the phases on the electron heating and sheath dynamics within one low frequency cycle is investigated using PROES and correlated with changes of ion energy distributions at the electrodes.

2:40pm **PS-ThA2 Spectroscopic and Beam Current Characterisation of an RF Excited Argon Plasma Cathode Electron Beam Gun for Material Processing Applications**, ***Sofia del Pozo,*** TWI Ltd. and Brunel University, United Kingdom of Great Britain and Northern Ireland*, C.N. Ribton,* TWI Ltd., United Kingdom of Great Britain and Northern Ireland*, D.R. Smith*, Brunel University

Details are given of a design of a novel RF excited plasma cathode gun that generates electron beams (EBs) for material processing applications including additive manufacturing, welding and cutting. Plasma EB sources offer solutions to the main problems with conventional electron beam guns, which use a thermionic cathode. Cathode wear from thermal cycling or ion bombardment is eliminated. EB power can be controlled by RF power modulation, which avoids the need for a grid electrode, and as a result reduces beam aberration. This technology has generated interest from various sectors of industry including additive manufacturing where rapid printing would be possible due to the high power provided by the electron beam, and at the same time fast beam pulsing can control material melting.

In this work, EBs were generated at accelerating potentials between 30 kV and 60 kV with beam powers of up to 1kW. The experimental setup allowed carrying out optical emission spectroscopy measurements simultaneously with beam current measurements.

A capacitively coupled plasma was generated in a cylindrical quartz chamber with 14 mm inner diameter. An RF power signal of 20 to 50 W at 84 MHz was applied between electrodes separated by 25 to 80 mm. Electrons were extracted from the plasma chamber to the vacuum chamber (at about 10^{-5} mbar) through an aperture (0.8 to 1.2 mm diameter) at the end of the plasma chamber by applying an accelerating voltage. Typically argon was used but EBs were also generated using krypton, helium and air. The pressure in the plasma chamber was controlled in the range 0.1 mbar to 1.5 mbar.

Optical emission spectroscopy measurements have been carried out in order to optimise plasma parameters for higher electron emission. This plasma diagnosis technique was selected as it is non-intrusive and allows estimation of important plasma parameters such as electron density and temperature. The spectra were correlated with electron emission. Ar – II lines were found to be much intense than Ar – I lines in those plasmas of higher electron emission. It was observed that the electron beam power was increased as the plasma chamber pressure decreased in one of the plasma chamber geometries. At any one plasma pressure, the beam power increased with RF power.

Further work is currently being carried out in order to increase the power of the electron beams generated. This includes revised plasma chamber designs and particle in cell simulation of the argon plasma.

3:00pm **PS-ThA3 Around the World of RF-Plasma Generation: A Brief Tour in 80 (half) Minutes**, ***Neil Benjamin***, Lam Research Corporation **INVITED**

This paper starts with a review of historical progress to reach the present day, when it is virtually universal to use RF excited plasmas to process semiconductor materials. This may extend to hundreds of process steps as Deposition, Etching, Stripping, Cleaning and Surface treatments are all in the RF-plasma repertoire. In order to do so, multiple factors and timelines have had to converge, including:

I. Electronics development, specifically RF technology and devices.

II. Plasma Technology A.K.A. Gaseous Electronics, specifically Dry Processing as applied to: Semiconductors, Flat panel displays, P-V solar panels, MEMs devices etc.

It is less than 70 years since the invention of active solid state electronics in 1947, but the semiconductor industry is now mature and consolidated while continuing to advance according to Moore's law. In the same period RF delivery systems have also progressed from high power vacuum tubes/valves to solid state devices in the 1980s. Most such RF systems use 50Ω transmission lines (for I.S.M.) so that matching networks are used to optimize power transfer to the antenna load impedance. Plasma technology use for semiconductor production did not start until the late 1960s / early 70s. In particular, despite the engineering complications of dealing with RF excitation, RF plasmas became popular because of their suitability for use with dielectric materials, and ameliorating the potential for damage caused by passing DC currents through delicate devices during manufacture.

In the second half of the paper we consider that while the technology involved in plasma processing has remained basically the same for nigh on 50 years, the demands on RF performance, control and consistency have escalated beyond all recognition. I will address some typical RF-plasma issues with examples taken from the current state of the art that continue to challenge us. These include igniting and delivering RF into the changing load impedance of a transient plasma, whether due to instability or by design. Another is dealing with the problem of stable and consistent excitation when there are multiple frequencies present either due to multiple source frequencies or due to the plasma generation of harmonics and mixing products. I will discuss how we achieve stable performance in terms of both uniformity and tool matching, in part by using sensor based control schemes. The question we must answer going forward is whether we can maintain or indeed improve this level of precision and performance, but do so ever more cost effectively.

4:00pm **PS-ThA6 Electron Beam Generated Plasmas Produced in Fluorine-Containing Gases: Characterization of Plasma-Surface Interactions***,* ***Scott Walton****, D.R. Boris,* US Naval Research Laboratory*, R.F. Fernsler,* Sotera Defense Solutions, Inc.*, S.C. Hernández, Tz.B. Petrova, G.M. Petrov*, US Naval Research Laboratory

Electron beam generated plasmas are characterized by high plasma densities (> 10^{10} cm^{-3}) and very low electron temperatures (< 1 eV), making them well-suited for next-generation processing techniques, where high fluxes of low energy ions are desirable. In this work, we focus on characterizing the flux of species incident to substrates located adjacent to magnetically collimated electron beam generated plasmas produced in fluorine-containing gases (e.g. SF_6, C_xF_y, etc). In particular, the type and energy of the ions at the substrate surface are measured as function of relative gas concentration and substrate-to-beam distance. These results are complimented by bulk plasma measurements and modeling and then discussed in terms of the changes in surface directed ion flux caused by changes in electron temperature and density, and electronegativity associated with the introduction of attaching gases to very low T_e plasmas. This work is supported by the Naval Research Laboratory Base Program.

4:20pm **PS-ThA7 Electron Beam Generated Plasmas Produced in Fluorine-Containing Gases: Characterizing Plasma Parameters***,* ***David Boris****, G.M. Petrov,* Naval Research Laboratory*, R.F. Fernsler,* Sotera Defense Solutions*, Tz.B. Petrova, S.G. Walton*, Naval Research Laboratory

Electron beam generated plasmas are characterized by high plasma density (>10^{10} cm^{-3}), and very low electron temperatures (<1 eV) making them well suited to next generation processing techniques where high fluxes of low energy ions are desired. In this work, we focus on the characteristics these plasmas in fluorine containing chemistries (SF_6, C_xF_y), due to their relevance to industrial etching applications. In particular we focus on the effect of dilute fluorine gas mixtures on the electron density, total plasma density, electronegativity, and electron temperature. These parameters are measured using a suite of probes, with plasma parameters calculated using an NRL developed Langmuir probe model which is particularly useful in complex multi-component plasmas. The results are then compared with a one-dimensional steady-state hydrodynamic model of electron beam generated Ar-SF_6 plasmas at low pressure in a constant magnetic field.

This work supported by the Naval Research Laboratory Base Program

4:40pm **PS-ThA8 Microwave Plasma Source Technologies: A Fifty Year Evolution from Unwanted Discharges to Free Radical Sources, to Low Pressure and Temperature Plasma Processing, to Gem Quality Diamond Synthesis**, ***Jes Asmussen***, Michigan State University **INVITED**

Opportunities to create, to experiment with and to apply microwave plasmas occurred after world war II when high power microwave sources became commercially available. The first applications of microwave plasmas used a small, micro plasma - like discharge as a harmonic generator, i.e. these plasmas were used to generate even higher frequency electromagnetic radiation. As the understanding of how to efficiently create and maintain a discharge improved, microwave plasma sources, as they were identified at that time, were applied to numerous high and low pressure applications such as down stream and in - plasma free radical sources for thin film deposition, etching and more generally to a large variety of plasma surface treatments. Under the influence of these applications, microwave applicator and plasma source technologies rapidly evolved and became more application specialized. Initially a plasma discharge scale up was identified as a challenge, but the ability to produce large, high density microwave discharges was demonstrated. Completely new subclasses of microwave discharges, such as electron cyclotron resonance (ECR) discharges, were identified. Eventually applications, such as microwave plasma - assisted synthesis of diamond, created important new microwave plasma technologies. Certainly over the past fifty years microwave plasma sources have evolved into an important and diverse group of technologies that have broad range of material processing applications.

In this presentation, the historical evolution of microwave plasma source technologies will be briefly reviewed. The current diverse group of the technologies now known as microwave plasma source technologies will be organized into subclasses. The physics and the methods of efficiently coupling microwave energy to both high and low pressure discharges will be identified and compared. The state - of - the - art applications such as single crystal diamond synthesis and ECR discharges will be reviewed. Finally the current microwave plasma source technologies will be compared with the more common, lower frequency excited capacitive and inductive plasma sources.

5:20pm **PS-ThA10 Insights to Scaling Remote Plasma Sources Sustained in NF$_3$ Mixtures**, ***Shuo Huang***, University of Michigan, *V. Volynets, S. Lee, I.-C. Song, S. Lu,* Samsung Electronics Co., Ltd., Republic of Korea, *J.R. Hamilton, J. Tennyson,* University College London, UK, *M.J. Kushner*, University of Michigan

Remote plasma sources (RPS) are used in microelectronics fabrication to produce fluxes of radicals for etching and surface passivation in the absence of damage to devices that may occur by charging and energetic ion bombardment. RPS reactors use distance, grids or other discriminating barriers to reduce or eliminate charged particle fluxes from reaching the surface of the material being treated. Nitrogen trifluoride (NF$_3$) is often used in RPS due to the efficiency with which F atoms are produced by dissociative attachment. RPS sustained in NF$_3$ gas mixtures, such as Ar/NF$_3$/O$_2$ increases the variety of reactive species produced, for example, N$_x$O$_y$. For certain applications it may be desirable to separately optimize, for example, F atom fluxes; and O atoms, or N$_x$O$_y$. This separate optimization could, in principle, be performed using pulsed power or pulsed gas sources. In this paper, we report on a computational investigation of RPS sustained in different NF$_3$ containing gas mixtures using pulsed power for low-damage plasma etching applications. Two modelling approaches were used – global modelling to investigate fundamental reaction mechanisms and 2-dimensional modelling to address the spatial dynamics of flow. A reaction mechanism was developed for plasmas sustained in mixtures containing Ar/NF$_3$/N$_2$/O$_2$. Cross sections for NF$_x$ were generated using ab initio computational techniques based on the molecular R-matrix method. Results for RPS produced by both continuous wave power and pulsed power will be discussed, and comparisons made to experiments.

Selective Deposition as an Enabler of Self-Alignment Focus Topic
Room: 210F - Session SD+AS+EM+PS-ThA

Process Development for Selective Deposition and Self-aligned Patterning
Moderator: John Ekerdt, The University of Texas at Austin, Chuck Winter, Wayne State University

2:20pm **SD+AS+EM+PS-ThA1 Surface Chemistry Related to Selective Deposition**, ***Suvi Haukka***, ASM Microchemistry Ltd., Finland, *J.W. Maes*, ASM Belgium **INVITED**

The shrinking device dimensions in semiconductor manufacturing call for new innovative processing approaches. One of these considered is selective deposition which has gained increasing interest among semiconductor manufacturers today. Selective deposition would be highly beneficial in various ways, for instance, it would allow a decrease in lithography and etch steps reducing the cost of processing and enable enhanced scaling in narrow structures making bottom up fill possible. Chemical vapor deposition (CVD) and especially atomic layer deposition (ALD) as very surface sensitive techniques are considered enabling techniques.

Selective deposition typically deals with a selective deposition method where, for instance, a metal layer is selectively deposited on metal surface over dielectric surface, or a dielectric layer is selectively deposited on hydrophilic polymer over a more hydrophobic polymer. In most of the selective deposition schemes of today the passivation is used for the surface on which no deposition is desired. The most known method is to use SAM´s (self-assembled monolayers) which are silicon compounds with long carbon chains. Besides the SAM passivation of surfaces also the clever selection of precursors with built-in selectivity in certain process conditions could be applied.

In this paper, the chemistry challenges in the various selective deposition approaches and passivation means are reviewed. In addition, results from the selective deposition of metal on metal over dielectric surface in a Cu capping application and from selective strengthening of DSA (direct self-assembly) layers are presented.

3:00pm **SD+AS+EM+PS-ThA3 Selective Deposition - The New Patterning Paradigm?**, ***Florian Gstrein***, Intel Corporation **INVITED**

Top-down patterning techniques based on optical lithography have made consumer electronics ever more powerful, ubiquitous and affordable. This is largely due to the ability of lithographic techniques to transfer trillions of mask features to wafers at defect densities approaching virtually zero in high-volume manufacturing. While the resolution of optical lithography tools is typically considered to be the main challenge for continued device scaling, it is actually accurate pattern placement, which has emerged as the biggest concern. Novel bottom-up patterning approaches such as selective deposition are needed to overcome shortcomings in pattern placement accuracy.

The talk will first outline the challenges patterning processes based on 193i pitch division and EUV lithography face in terms of alignment accuracy and how complementary patterning techniques such as selective deposition can reduce pattern placement errors. One of the great challenges of selective deposition is defect mitigation, especially as the sensitivity to killer defects increases as device dimensions scale. Defect mitigation requires a fundamental understanding of the chemical selectivity of surfaces. While molecules can recognize chemical functionality on a surface, selective deposition processes based on atomic layer deposition (ALD) or chemical vapor deposition (CVD) are exceedingly rare and largely limited to specific precursors and substrates. For metal deposition, inherent selectivity was achieved through judicious precursor ligand design. Experimental results will be presented in the context of a theoretical investigations aimed at calculating the kinetic barriers that govern the selectivity of metal deposition. The use of self-assembled monolayers (SAMs) as passivants and/or blocking layers for subsequent deposition is an attractive way of overcoming the non-selectivity of many CVD or ALD processes. Here, the critical parameters for selective blocking are choice of the terminal group, surface termination, carbon chain length, and proper precursor choice. Using SAMs, selective deposition of dielectrics with respect to a variety of surfaces was achieved. The talk will conclude with our vision of how defects can be mitigated: It comprises a fundamental understanding of the chemical nature of the surface, precursors with high kinetic barriers for defect formation, passivation of defect nucleation sites, and the removal of defects post deposition. Selective deposition, if properly resourced and developed, can provide powerful means to future scaling and is one way of ensuring that patterning will continue to support Moore's Law in the foreseeable future.

4:00pm **SD+AS+EM+PS-ThA6 Area-Selective Molecular Layer Deposition: Enhanced Selectivity via Selective Etching**, ***Richard Closser***, *D.S. Bergsman, F.H. Minaye Hashemi, S.F. Bent*, Stanford University

Recent developments in electronic devices are pushing toward smaller and smaller features of both metal and dielectric patterns, along with a desire to produce selectively deposited organic thin films on such patterns. Techniques that allow for a high degree of control over the thickness and conformality of organic thin films, such as molecular layer deposition (MLD), are ideal candidates to meet these selective deposition requirements. Using MLD, several types of thin film polymers can be deposited with angstrom-level control due to the sequential, self-limiting surface reactions resulting in monomer-by-monomer growth. Selectivity in the MLD polymer growth is then achieved by utilizing the chemical functionally between the solid substrate surface and the gas phase monomer precursors.

Previously, we have shown the ability to selectively deposit thin film polymers by MLD onto pre-patterned metal and dielectric substrates by utilizing a blocking layer of octadecylphosphonic acid (ODPA) self-assembled monolayers (SAMs) that deposits onto metals more readily than onto dielectric films. Although this process can prevent MLD for up to 6 nm of deposition, selectivity of polymer growth is lost for thicker films, and therefore we are exploring new methods for increasing the MLD selectivity. For the current studies, ODPA SAM is deposited onto a patterned metal/dielectric (Cu on SiO$_2$) substrate to act as the MLD blocking layer. Once the SAM is fully deposited, polyurea films are grown onto the substrate by MLD to a desired thickness which can be controlled by the number of monomer dose cycles used. An acid etchant is then used to remove the surface oxide of the metal along with the SAM layer while leaving intact the polymer film deposited onto the dielectric. X-ray photoelectron spectroscopy, Auger electron spectroscopy, and ellipsometry measurements show that this process removes undesired MLD film that was deposited on the metal. Studies on patterned substrates confirm selective polymer film growth onto the dielectric over the metal. The etchant removal technique thus increases the selectivity of MLD growth by more than an order of magnitude when compared to the SAM blocking layer alone. Due to the increased selectivity with the etching based process, selective deposition of MLD films as thick as 12 nm have been demonstrated. Atomic force microscopy results show slight surface roughening due to etching while the bulk of the metal/dielectric pattern remains intact. This increase in MLD selectivity should allow for novel applications of selective polymer film deposition.

4:20pm **SD+AS+EM+PS-ThA7 Nucleation and Steady State ALD of Metallic Tin Using $SnCl_4$ and a Silyl Pyrazine Reducing Agent**, ***Eric Stevens***, *M.B. Mousa, G.N. Parsons*, North Carolina State University

Metal atomic layer deposition (ALD) processes are typically limited to noble, high work-function metals where uniform nucleation and conformal growth can be problematic. Recent work suggests that 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (DHP) could be an effective reducing agent for deposition of metals with highly negative electrochemical potentials. This work investigates DHP as a potential reducing agent for tin metal ALD using tin (IV) chloride ($SnCl_4$).

Experiments were carried out in a custom-built, hot-wall reactor using N_2 carrier gas, an operating pressure of 1.3 Torr, and temperatures between 130 and 170°C. The DHP source was heated to 70°C to maintain a vapor pressure ~1.2 Torr. Initial films were deposited at 130°C on silicon using a $SnCl_4/N_2/DHP/N_2$ exposure sequence of 4/50/10/50 seconds, then analyzed ex-situ by X-ray photoelectron spectroscopy (XPS) with Ar depth profiling. In sputtering deeper into the film, XPS exhibited both Sn-Sn and Sn-O peaks at 485 and 486.7 eV, respectively, where a decrease in Sn-O and an increase in Sn-Sn peak intensities suggests native oxidation of the film upon exposure to air. Furthermore, 7% Cl and 19% N were found in the films after sputtering, presumably from an incomplete reaction and/or incorporation of reaction byproducts.

To better understand surface reactions and growth mechanisms, we characterized the ALD process at 130, 150, and 170°C using *in situ* quadrupole mass spectrometry (QMS) and quartz crystal microbalance (QCM). QCM analysis at 130 and 150°C showed continued growth with extended exposures, consistent with non-ALD growth. Deposition at 170 °C was more repeatable and more closely approached surface saturation. At 170°C, QCM showed a clear mass increase during the $SnCl_4$ dose and a corresponding mass decrease during the DHP dose, consistent with DHP removing Cl and reducing the Sn-Cl surface. Moreover, the QMS results showed peaks exclusively during DHP doses at m/z values of 80 (pyrazine) and 65, 93, 95 (trimethylsilyl chloride), which are the most probable byproducts of DHP reacting with a chlorinated surface.

Using gold-coated QCM crystals at 170°C, Sn growth proceeds slowly for the first ~150 ALD cycles, whereas growth on QCM crystals previously coated with Sn show a more rapid transition to steady-state growth (<20 cycles). We are currently investigating the nucleation on different substrates and how process conditions can be tuned to achieve selective deposition. Understanding the surface reaction and growth mechanisms of tin metal deposition using DHP could provide a foundation for deposition of metal thin-films that were previously unattainable.

4:40pm **SD+AS+EM+PS-ThA8 Determination of the Minimum Saturating Dose during Atomic Layer Deposition of Alumina and Titania on Si(100) and Si(100)-H**, *D. Dick*, University of Texas at Dallas, ***Joshua Ballard***, *J. Randall*, Zyvex Labs, *Y.J. Chabal*, University of Texas at Dallas

Atomic layer deposition (ALD) has become an important process step in semiconductor manufacturing, where the self-limiting nature of each step of the process permits atomic scale control over the ultimate layer thickness in addition to relatively fast processing with high pressure reactors. However, it has been shown that ALD can be used to selectively deposit material onto patterned surfaces, requiring not only saturation of each deposition cycle in desired areas but also suppression of deposition in those areas where it is undesirable. One mechanism for improving practical selectivity would be to find the minimum exposure that is saturates the growth where desired in order to avoid excess overall reaction probability in areas where inhibited growth is preferred.

To investigate this, we have examined the deposition in vacuum ("UHV ALD") of Al_2O_3 and TiO_2 with TMA and $TiCl_4$, respectively, on both hydrophobic, H-terminated Si(100) surfaces and hydrophilic OH-terminated Si(100) surfaces prepared by H_2O exposure of clean Si(100)-(2x1) surfaces. Surface reactions and relative coverages are determined by in-situ IR spectroscopy, and ex-situ XPS. We find that good selectivity can be achieved at 150°C. Preliminary data and calculations also suggest that an initial wetting layer of TMA on clean Si(100) promotes subsequent growth of TiO_2 or other high-k dielectrics. Finally, we will discuss how these findings have made it possible to develop a full multi-cycle process for a custom low-pressure ALD system equipped with scanning tunneling microscopy and atomic force microscopy.

5:00pm **SD+AS+EM+PS-ThA9 Selective Growth of GeSbTe Phase-Changing Materials Utilizing Self-Aligned Confined Structure**, ***ByungJoon Choi***, Seoul National University of Science and Technology, Republic of Korea, *T. Eom, C.S. Hwang*, Seoul National University, Republic of Korea

GST Phase changing material, typically GeTe–Sb_2Te_3 pseudo-binary solid solution, has been extensively studied for rewritable digital versatile optical disks or phase change random access memory (PcRAM), on account of the drastic change of its optical reflectivity or electrical resistivity between amorphous and crystalline phases. As the device size of PcRAM is scaled down, GST materials should be confined into the contact-plug for reducing its programming current, which cannot be achieved by any physical deposition method.

Among the various metal-organic (MO) precursors, the combination of $Ge(iBu)_4$, $Sb(iPr)_3$ and $Te(iPr)_2$ has been extensively studied for plasma enhanced chemical vapor depostion or its variant methods with plasma-activated H_2 gas as a reducing agent of the MO-precursors. Plasma-enhanced pulsed CVD was attempted using the precursor pulse sequence consisting of Sb–Te–Ge–Te cycles (each elemental cycle is composed of precursor injection and Ar + H_2 plasma reduction steps). The chemical composition of the films was appropriately controlled by the cycle ratio and sequence of each precursor pulse. The linear growth with the number of cycles was shown, and the GPC (growth-per-cycle, i. e. growth rate) was determined to be 0.73 nm/super-cycle from the slope at a wafer temperature of 200°C.

Strong substrate dependency can be utilized in the selective growth of GST material on a TiN contact-plug formed in the SiO_2 inter-layer dielectric (ILD). Higher selectivity (difference of GPC) between TiN contact-plug and SiO_2 ILD layer was achieved by pulsed CVD with increasing the amount of $Te(iPr)_2$ injection. The reason for the selective growth was believed to have originated from the adverse interference of the residual gas (unreacted $Te(iPr)_2$ or its derivatives) to the chemical adsorption of Sb nuclei on the SiO_2 surface, which functions as a nucleation site for further GST growth. It was reported that amide-based Ge precursors also showed strong selectivity at a particular temperature, enabling Sb and Te precursors to be chemisorbed on the Ge seed layer, which could be utilized for selective growth of GST.

The most feasible explanation for the substrate-dependent growth behavior of the GST film is the electron donation from the substrate, which would enhance the precursor decomposition and removal of ligands from the adsorbed precursor molecules. The nucleation and growth behaviors of the GST films were studied on Si substrates with various nucleation or buffer layers. It turned out that the types of substrates have a crucial impact on the nucleation behaviors and the chemical composition of the film.

5:20pm **SD+AS+EM+PS-ThA10 Toward an All- Vapor Process for Area Selective Atomic Layer Deposition**, ***FatemehSadat Hashemi***, *S.F. Bent*, Stanford University

Modern electronic devices containing planar and 3-D structures utilize a number of metal/dielectric patterns in both the front and back end. The scaling of next generation electronic devices makes achieving these patterns increasingly difficult and motivates the development of novel processing methods. One such method−area selective deposition−has the opportunity to play an important role in significantly reducing process complexities associated with current top-down fabrication of patterned structures by eliminating some of the deposition and etching steps that are time-consuming and expensive.

Atomic layer deposition (ALD) is a good choice for area selective deposition because its chemical specificity provides a means to achieve selectivity on a spatially patterned substrate. Area selective ALD, reported previously by several groups, requires improvements for the process to be compatible with current device fabrication goals. Most previous studies of area selective ALD have achieved deposited thicknesses on the order of only a few nanometers and the selectivity was generally obtained by passivation of the surface using self-assembled monolayers (SAMs) in the regions where ALD was not desired. Existing methods are usually performed by dipping the substrates into a solution containing the SAM-forming molecules for several hours. A more desirable all-vapor process would require vapor delivery of the SAMs. This method would provide better SAM coverage on porous or three-dimensional structures, potentially decreasing the required deposition time for the passivation layer, and allowing the SAM passivation step to be integrated with the rest of the ALD process.

In this work, we investigate area selective dielectric-on-dielectric deposition by selectively depositing organic alkanethiol SAM as the blocking layer on metal parts of a metal/dielectric (Cu/SiO_2) pattern. We compare area-selective ALD achieved by introduction of the thiolate SAM in both the solution and vapor phase. We show that while in both cases the SAM can prevent subsequent deposition of metal oxide dielectric films via ALD, vapor deposition provides stronger passivation in a shorter exposure process on the metal. We also report results on regenerating the thiol SAM protecting layer from the vapor phase between ALD cycles and show that this approach is effective in improving the blocking properties of the SAM on Cu. This strategy provides the ability to significantly improve selective deposition of dielectrics. Moreover, it is a significant step toward an all-vapor process for area selective deposition, opening up the possibility for new applications in next generation electronic devices.

5:40pm **SD+AS+EM+PS-ThA11 Selective Deposition of ALD Metal oxides and Metal Thin Films by Fab-Friendly Surface Treatments**, ***Kandabara Tapily***, *K.-H. Yu, S. Consiglio, R. Clark, D. O'Meara, C. Wajda, G. Leusink*, TEL Technology Center, America, LLC

For the last 5 decades, the semiconductor industry has relied on the continued scaling down of the device feature size in order to improve performance and increase bit density according to Moore's law. However, with the delay in implementation of extreme ultraviolet lithography (EUV) in high volume manufacturing,[1] patterning beyond the 14 nm technology node is getting extremely difficult to manage due to the overlay control and the increase in manufacturing cost due to multi-layer alignments. In order to keep reducing the device feature size, new patterning solutions are needed such as selective deposition and selective etching of materials. Atomic layer deposition (ALD) has emerged as one of the leading film deposition techniques as a result of the semiconductor device scaling.[2] ALD provides excellent film control, uniformity and high conformality. ALD is highly surface reaction driven and it is possible to modify the substrate surface to activate or deactivate growth on selected area hence selective-area ALD (SA-ALD). Selective-area ALD can simplify and reduce the high manufacturing cost associated with highly aggressive patterning schemes by eliminating certain lithography steps. Thin films can now be selectively deposited or removed from a desired area. Most selective-area ALD studies in the literature are conducted with the use of self-assembled monolayers (SAMs) in order to deactivate or activate growth on certain areas.[3-5] SAMs are thin organic films that form spontaneously in tightly packed oriented molecules on solid surfaces. A key enabler of SAMs is the ability to turn these organic layers into patterned layers. However, thermal stability and the slow formation process into well packed layer are some of the major drawbacks of SAMs.[5]

In this study, a non SAMs based approach was used to inhibit ALD growth of metals and metal oxides. Using different surface treatments, it was observed the growth of the ALD thin films can be modulated, see Fig.1 and Fig.2 respectively. ALD Al_2O_3 growth was suppressed by a combination of the vapor HF and cyclical low temperature plasma hydrogen treatment and deposition. Additionally, ALD TaN growth was also inhibited by the use of a combination trimethylsilane (TMS) and dimethylamine (DMA) treatment of the surface prior to ALD deposition.

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Surface Modification of Materials by Plasmas for Medical Purposes Focus Topic

Room: 211D - Session SM+AS+BI+PS-ThA

Plasma Processing of Biomaterials and Biological Systems

Moderator: David Graves, University of California, Berkeley, Jean-Michel Pouvesle, GREMI CNRS/Université d'Orléans

2:20pm **SM+AS+BI+PS-ThA1 Matching Plasma Sources with Intended Biomedical Outcomes: Open Questions in Modeling of Plasma Surface Interactions**, *W. Tian,* University of Michigan, *S.A. Norberg,* US Military Academy - West Point, *A.M. Lietz,* University of Michigan, *N.Yu. Babaeva,* Joint Institute for High Temperatures, ***Mark Kushner***, University of Michigan **INVITED**

Plasma surface modification of materials for biomedical applications typically involves atmospheric pressure plasmas in the form of dielectric barrier discharges (DBDs) or atmospheric pressure plasma jets (APPJs). In many cases, APPJs operate similarly to DBDs with an ionization wave (IW) propagating through a rare-gas dominated gas channel. The intersection of the IW with the surface being treated, for example tissue, in both DBDs and APPJ produces locally large fluxes of ions, UV/VUV photons and electric fields onto the surface. These fluxes are collectively *hard fluxes* due to the higher levels of activation energy they represent. Remote DBDs and APPJs where the plasma plume does not intersect the surface produce *soft fluxes*, dominated by neutral reactants. The character and ratios of *hard-to-soft fluxes* and their compositions are functions of flow dynamics, ambient conditions (e.g., humidity) and pulse power waveforms. In many biomedical applications, the tissue is covered by a liquid (or the intended surface is liquid as in plasma activated water). In these cases, plasma produced activation energy, radicals and ions must penetrate through the plasma-liquid interface, where liquid phase mechanisms then determine the reactants to the tissue. From one perspective, significant advances have been made in modeling these processes and furthering our understanding. From another perspective, there are still significant open questions that models need to address, including the manner of coupling of the gas phase plasma and liquid, gas induced fluid dynamics, long term evolution of the liquid chemistry, reactions at the surface of the tissue and control schemes to minimize variability. A brief overview of progress in modeling plasma modification of biomaterials will be provided followed by examples of the authors' modeling works for APPJs and DBDs intersecting with model tissues and liquids.

3:00pm **SM+AS+BI+PS-ThA3 Plasma Processing of Biomimetic and Sintered Calcium Phosphates for Bone Regeneration and Repair**, ***Cristina Canal***, Technical University of Catalonia, Spain **INVITED**

Large bone defects caused by trauma, osteoporotic fractures, infection and tumour or cysts resection pose a great clinical and socio economic problem. Bone grafting materials respond to the need generated by over 2 million bone grafting procedures that are performed every year worldwide. As an alternative to autografts or xenografts, different biomaterials have been proposed, yet with partial success since different aspects remain yet to be improved.

In this context, the use of low pressure (LP) and atmospheric pressure (AP) plasmas opens new opportunities in the field of bone biomaterials. It is the aim of this talk to provide an overview on the strategies undertaken in our group to enhance diverse features of bone biomaterials and to enhance bone therapies.

The examples discussed here include biomimetic hydroxyapatite (HA) and β-tricalcium phosphate (β -TCP) as the most clinically used calcium phosphate (CaP) ceramics for bone regeneration. Some of the points of improvement include increasing their mechanical strength, or using them as local dosage forms for the delivery of drugs, to aid in different therapies, such as combating infection or fighting cancer.

For instance, we have investigated LP plasmas with the aim of expanding the use of biomimetic CaPs to load-bearing sites. Although composites have been defined, their performance is not yet optimal, possibly due to insufficient adhesion between the matrix and the reinforcing agent. Oxygen and argon plasmas have been employed in the surface modification of polylactide fibers to improve the adhesion at the interface between them and biomimetic CaPs with interesting results.

In a different approach we have focused on modulating drug delivery from bone biomaterials. Both AP and LP plasmas are of interest with views on different medical applications and in the design of advanced biomaterials with controlled drug release properties. Different strategies are considered with that aim, such as using either plasma functionalization with AP plasma jet to modulate the interactions of the drug with the CaP surface or employing LP plasma polymerization on CaP scaffolds as a strategy to control the drug release. Lastly, AP plasmas are in the limelight due to their wide potential in the medical field, and here we will discuss some recent findings for application in bone therapies and regeneration.

Acknowledgements

Spanish Government is acknowledged for support through Project MAT2012-38438-C03-01, co-funded by the EU through European Regional Development Funds, and Ramon y Cajal fellowship of CC. The European Commission is also acknowledged through funding in FP7/2007-2013 under the Reborne project (no. 241879).

4:00pm **SM+AS+BI+PS-ThA6 Plasma Processing of Biomaterials and Biomedical Devices**, *H.J. Griesser, T.D. Michl, S.S. Griesser, M. Jasieniak, H.H. Mon, **Bryan Coad***, University of South Australia **INVITED**

Gas plasmas have attracted considerable attention over more than 40 years as a convenient method for changing the surface chemical composition of biomaterials and thereby alter and control the interfacial interactions between biomedical devices and contacting "biology" such as protein solutions, blood, cells and tissue, and bacterial biofilm growth. Plasma technologies are already in use on a large industrial scale in several biomedical device companies; for example 30-day contact lenses use a thin plasma coating to confer wettability and low fouling to silicone-based contact lens materials. Bio-interfacial interactions are very short range, and hence it is sufficient to apply ultrathin coatings (< 20 nm thick). Plasma techniques are ideally suited because process control is straightforward and the resultant surface modifications or coatings tend to have a high degree of uniformity and reproducibility compared with other, solution based coating methods. On the other hand, the complex chemical composition of plasma gas phases prevents fine control of chemistry to the extent achievable by conventional chemical approaches. Detailed surface analysis is essential.

Plasma approaches are useful to produce coatings designed to combat the problem of bacterial and fungal biofilm growth on biomedical devices, which leads to infections and delayed healing. One approach is the use of organochlorine plasma polymer coatings, which are highly effective at contact killing. Other, cytocompatible approaches comprise the use of plasma polymer coatings that release NO or available antibiotics such as levofloxacin. A different approach entails the covalent immobilization of a monolayer of antimicrobial molecules onto a thin plasma polymer interlayer whose function is to provide good adhesion and reactive surface chemical groups that can be used to attach antibiotics. Such covalently grafted monolayers have given excellent deterrence of attachment and biofilm formation of bacteria and pathogenic fungi.

4:40pm **SM+AS+BI+PS-ThA8 Organs on a Chip – Biointerfaces in Stem Cell Research**, ***Kevin Healy***, University of California at Berkeley **INVITED**

Highly regulated signals in the stem cell microenvironment such as ligand adhesion density, matrix stiffness and architecture, and growth factor presentation and concentration have been implicated in modulating stem cell differentiation, maturation, tissue formation, and ultimately function. My group has developed a range of materials systems and devices to study and control stem cell function and their self-organization into three-dimensional microtissues (e.g., 'organs on a chip'). These systems are being developed for screening molecular therapies and patient specific medicine via *in vitro* disease specific tissue models. Examples of how biointerface science is important in these applications will be highlighted. The benefits of our approach include: 1) robust and reproducible platform embodies precision microengineering to create better microtissue environments; 2) precise delivery of molecules (e.g., drugs) in a computationally predictable manner; 3) ability to model human cardiomyopathy; and, 4) cost efficient and high content characterization of cardiac tissue drug response.

5:20pm **SM+AS+BI+PS-ThA10 Effect of the Radical Species for Gene Transfection by Discharge Plasma Irradiation**, ***Yoshihisa Ikeda**, M. Jinno*, Ehime University, Japan

Gene transfection is a technique of deliberately introducing nucleic acids into cells in order to give them specific characteristics. In practice, this can be achieved in three different ways: chemical method, physical method and the viral vector method.

One of the physical methods that uses discharge plasma irradiation was invented by Satoh, who is one of the authors, and his group in 2002. Since this technique is free from adverse effect associated with viruses, there are no risks as the others mentioned above. The plasma irradiation on genes and cells induces the transfection process in which the genes and cells are exposed to discharge current, charged particles and chemically reactive species.

The authors investigated the factors for plasma gene transfection by changing protocols and looked at the time periods the factors become effective. The results is that transfection rate drops to 1/10 of the standard protocol when the charged particles and chemically reactive species genes are washed out from the wells by PBS solution 60s after plasma irradiation. Since the life times of the charged particles delivered from plasma to the plasmid solution is less than 60s, the direct effect of the charged particles causing transfection finishes before wash out process. This means that nearly 1/10 of transfections occur during plasma irradiation and that the last 9/10 of transfections occur after plasma irradiation is stopped. This second stage transfection is mainly caused by the residual chemically reactive species, however, plasma irradiation stress to cells and plasmids also induces transfection., i.e. possibly charging effect and oxidation stress induce bio-chemical process of the cells in addition to the chemical reactions on the cell membrane and plasmid induced by chemically reactive species such as radicals.

5:40pm **SM+AS+BI+PS-ThA11 Nonlinear Optical Spectroscopic Observation of Plasma-Treated Bio-Specimen**, ***Kenji Ishikawa**, R. Furuta, K. Takeda,* Nagoya University, Japan*, T. Nomura, T. Ohta,* Meijo University, Japan*, H. Hashizume, H. Kondo,* Nagoya University, Japan*, M. Ito,* Meijo University, Japan*, M. Sekine, M. Hori*, Nagoya University, Japan

Applications of nonequilibrium atmospheric pressure plasma (NEAPP) to the medical field have been reported in recent years. However, a mechanism of interactions between NEAPP and living cells has not been yet elucidated comprehensively. Our strategy for elucidation of plasma-biomaterial interactions is to observe reactions *in situ* at real time. By applying nonlinear optical spectroscopic techniques, the vibrational sum-frequency-generation (SFG) and multiplex coherent anti-Stokes Raman scattering (CARS) microscopy, which are a beneficial tool for addressing best sensitivity at surface and interface, have been used in this study. By using SFG, we have explored topmost surface modification after the interaction between plasma and biopolymeric materials. For the NEAPP-induced reactions on budding yeasts as an eukaryotic cell model, a two-dimensional mapping of budding yeasts treated by the plasma using the CARS microscopy was observed with fluorescence label-free contrasts of chemical vibrational nature. The biomedical imaging of cell membranes, intracellular organelles, nucleus and so forth, was revealed to decompose intracellular membrane by exposure of plasma-generated chemically reactive species, especially for induction of lipid peroxidation. These results will be useful for understanding the plasma induced reactions in the plasma medicine.

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.

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 5*a*) 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 TiO_2(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

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*** Morton S. Traum Award Finalist**

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.

Surface Science
Room: 113 - Session SS+AS+EM+EN-ThA

Atomistic Modeling of Surface Phenomena & Semiconductor Surfaces and Interfaces - II
Moderator: Talat Rahman, University of Central Florida

2:20pm **SS+AS+EM+EN-ThA1 Ideas Old and New Applied to Non-Ideal Surface Adsorption and Reaction**, ***William Schneider***, University of Notre Dame **INVITED**

Free energies of adsorption are arguably the most elementary quantities in heterogeneous catalysis. These free energies depend on the surface and adsorbate (reactant, intermediate, or product) of interest, system temperature and adsorbate coverage. The free energy represents a balance between the energetic driving force for creating bonds between an adsorbate and a surface and the entropic cost of moving an adsorbate from a fluid phase to a surface. Standard density functional theory (DFT) approaches generally begin by optimizing the location of an adsorbate on a surface, computing a binding energy, and approximating the internal, translational, and configurational contributions to the free energy. In this work we examine the reliability of standard approximations and describe easily applied improvements that give reliable free energy estimates. We describe applications to adsorption at metal surfaces and in the pores of zeolites.

3:00pm **SS+AS+EM+EN-ThA3 Insights into the Oxidation of Stepped Cu Surfaces using Multiscale Investigations**, *Q. Zhu, W.A. Saidi,* ***Judith Yang***, University of Pittsburgh

Surface defects can induce non-canonical oxidation channels on metal surfaces that may lead to the formation of novel nanostructures. Recently, in situ environmental transmission electron microscopy (ETEM) experiments showed that the oxidation of stepped Cu surfaces promotes the formation of a flat metal-oxide interface through Cu adatoms detachment from steps and diffusion across the terraces. To bridge the gap between experiments and theory, we are investigating Cu oxidation using a multiscale computational approach. Our previous MD simulations based on a reactive force field (ReaxFF) demonstrated that the oxidation of stepped Cu(100) takes place on the upper terrace at a faster rate than the lower terrace due to a preferable oxygen diffusion from the lower to upper terraces. We have extended this study using first-principles density functional theory (DFT) and kinetic Monte Carlo (KMC), and performed a systematic study of all stepped Cu surfaces with a low Miller index. The DFT results show that the oxygen diffusion trend varies with the surface type, where in most cases the oxygen ascending diffusion is more favored. This result is confirmed also with ReaxFF MD and KMC simulations. The MD simulations, with a fine-tuned ReaxFF force field parametrization, have also indicated that oxygen adatoms on the upper terrace can enhance the interlayer Cu atom mass transport. These theoretical simulations provide essential fundamental understanding of the experimentally observed smoothing of the Cu surface during in situ oxidation.

3:20pm **SS+AS+EM+EN-ThA4 Reconciling Complimentary Analyses of Epitaxial Growth: Role of Transient Mobility for para-Hexaphenyl on Mica**, ***Josue Morales-Cifuentes***, *T.L. Einstein,* University of Maryland, College Park, *A. Pimpinelli*, Rice University

In studies of epitaxial growth, a major goal is to assess the size of the smallest stable cluster (with $i + 1$ monomers, where i is the critical nucleus size). This is accomplished by analyzing either the capture zone distribution (CZD), the scaling of incident flux F to the density of stable islands N or the island-size distribution (ISD). For CZD, generalized Wigner distributions (GWD) have proven useful, [1,2] with successful applications to, non-comprehensively: polar-conjugated molecule Alq_3 on passivated Si(100), self-assembled Ge/Si(001) nanoislands and para-Hexaphenyl (6P) films on amorphous mica. [3] We concentrate on the last, for which the Winkler group found that $i \approx 3$.

Scaling of N usually follows $N \propto F^{\alpha}$, where α is the growth exponent. For 6P films, a difference in scaling behaviors at small and large F is attributed to DLA and ALA dynamics (i.e. $i = 5 \pm 2$, and $i = 7 \pm 2$, respectively). [4] This discrepancy motivates our current work, where transient mobility effects modify scaling non-trivially. [5]

Consider that monomers begin in a (ballistic) hot precursor state before thermalizing (random walk). The competing times of ballistic monomers becoming thermalized vs. being captured by an island naturally define a "thermalization" scale for the system. We obtain an analytic solution and elaborate on the physical meaning behind the energies and dimensionless parameters used. Novel scaling regimes are retrieved for which power-law scaling applies, with non-monotonic crossovers between them and the growth exponent exclusively dependent on i. Applying the model to the 6P films results in good agreement for the scaling and the activation energies: experimental values of the activation energies of 0.26eV (high-T) and 0.04eV (low-T) match model predictions of 0.3eV (high-T) and 0.04eV (low-T). Furthermore, the high-flux regime is interpreted not as ALA (attachment-limited aggregation) or HMA (hot monomer aggregation) but rather as an intermediate scaling regime related to DLA (diffusion-limited aggregation). Lastly, we discuss a simplifying approximation for the model and connections to some capture zone distribution considerations of α. [6]

[1] T.L. Einstein, A. Pimpinelli, D. González, J. Cryst. Growth 401, 67 (2014)

[2] T.L. Einstein, A. Pimpinelli, D. González, and J. R. Morales-Cifuentes, Proc. CCP2014, J. Phys.: Conf. Series (2015), in press.

[3] T. Potocar, G. Lorbek, D. Nabok et al. 2011 Phys. Rev. B 83 075423

[4] L. Tumbek & A. Winkler, Surf. Sci. 606, L55 (2012)

[5] J. R. Morales-Cifuentes, T. L. Einstein, and A. Pimpinelli. Phys. Rev. Lett. 113, 246101(2014)

[6] J. R. Morales-Cifuentes, T. L. Einstein, and A. Pimpinelli (in preparation)

4:00pm **SS+AS+EM+EN-ThA6 Probing 2-DEG at InN Surface by Electrolyte-Gated Raman Spectroscopy**, *E. Alarcon Llado,* Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, ***Tommaso Brazzini***, Lawrence Berkeley Lab, University of California, Berkeley, *J.W. Ager*, Lawrence Berkeley National Laboratory (LBNL)

Indium nitride has attracted much attention as its narrow bandgap (~0.67eV) expands the range of the direct gaps of the group III-N alloys into the visible and near-IR and thus offers an outstanding potential for solar energy conversion and optoelectronic applications. However, experimental demonstration of high efficiency In-rich III-V pn rectification junctions has been hampered by the existence of an intrinsic interface electron accumulation layer, which seems to persist regardless of surface treatment. The large capacitance of the Helmholtz double layer that forms on a surface of an object in contact with an electrolyte allows the 2-DEG at the surface of InN to be tuned and even depleted. Using this effect, we demonstrated the first pn rectification behavior in InN.[1]

In addition, the 2-DEG accumulation layer affects not only the electrical properties, but also has brought many controversies in the interpretation of optical experiments. Raman spectroscopy probes not only the lattice dynamics in a crystal, but also the electronic structure and free carriers. In particular, the interaction between the free electrons at the surface and the longitudinal optical (LO) phonon in InN has been addressed by several studies. However some questions still remain.

In this work, we present an in-situ micro-Raman study that confirms the presence of a surface related Raman mode in InN and shows its interaction with accumulated electrons at the surface. Electrolyte gated Raman spectroscopy (EGRS) on InN layers was performed in order to modulate and in-situ probe the surface electron accumulation region in InN. A reversible shift of the LO phonon with the applied gate potential is found (see figure 1). The peak position and shift depends on the probing light energy, however it is independent of bulk doping. We explain these findings by Martin's double scattering mechanism and bandgap narrowing at the surface tuned by the gate voltage. InN nanocolumns were also investigated by EGRS. The LO mode lies at higher frequencies in all nanocolumn samples. This fact corroborates the nature of the scattering mechanism, which is strongly dependent on the surface orientation. In summary, our results clearly demonstrate the surface origin of this feature and allow the fundamental study and understanding of the electronic structure of InN.

1.Alarcón-Lladó, E. et al. PN junction rectification in electrolyte gated Mg-doped InN. Appl. Phys. Lett. 99, 102106 (2011).

4:20pm **SS+AS+EM+EN-ThA7 Surface Termination of Single Crystal Bi_2Se_3 Investigated by Low Energy Ion Scattering**, ***Weimin Zhou**, J.A. Yarmoff*, UC Riverside

Bismuth Selenide (Bi_2Se_3) is a prototypical topological insulator (TI) with a two-dimensional layered structure that enables clean and well-ordered surfaces to be prepared by cleaving. Although some surface structure studies have concluded that the cleaved surface is terminated with Se, as is expected from the bulk crystal structure, there are other reports that show either a Bi- or mixed-termination [1]. Low Energy Ion Scattering (LEIS) and low energy electron diffraction (LEED) are used here to compare surfaces prepared by *ex-situ* cleaving, *in-situ* cleaving and Ar^+ ion bombardment and annealing (IBA) in ultra-high vacuum. Surfaces prepared by *in-situ* cleaving always have a sharp 1x1 LEED patterns and are Se-terminated. Surfaces prepared by IBA show a transition from Bi- to Se-termination with increasing annealing temperature. Samples inserted into the vacuum chamber following *ex-situ* cleaving have much dimmer LEED patterns, show surface contamination with Auger electron spectroscopy, and could be terminated either with Se or Bi. The angular dependence of LEIS spectra, which is sensitive to the surface atomic structure, doesn't indicate any substantial differences between surfaces prepared by IBA or *in-situ* cleaving. Ion scattering simulations using Kalypso are compared to experimental angular data to obtain more details about the structure. Exposure of clean surfaces to gaseous species will also be discussed in an effort to determine the surface chemical reactions responsible for the termination change.

[1] X. He, W. Zhou, Z. Y. Wang, Y.N. Zhang, J. Shi, R.Q. Wu and J.A. Yarmoff, Phys. Rev. Lett. **110**, 156101 (2013).

4:40pm **SS+AS+EM+EN-ThA8 Real-Time Imaging with Atomic-level Spatial Resolution of Silicon Oxidation**, ***Bryan Wiggins**, L.G. Avila-Bront, R. Edel, S.J. Sibener*, University of Chicago

The investigation of the initial stages of molecular oxygen adsorption on Si(111)-7x7 with real-time and real-space visualization will be discussed in this presentation. We will present the first results from a newly built supersonic molecular beam paired with a scanning probe microscope instrument. The system is designed with an oil free differentially pumped supersonic beam and has a custom scanning probe microscope with the surface plane normal to the beam. This geometric arrangement allows us to perform real-time and real-space *in-situ* experiments. This study consists of exploring the potential energy surface for molecular oxygen adsorption on Si(111)-7x7. The questions that are being addressed are fundamental for issues relating to semiconductor oxidation as well as being of direct relevance to semiconductor processing. The site-specific locations of molecular oxygen reactivity on Si(111)-7x7 surfaces are not clear and remains a topic of current discussion. Recent spectroscopic studies show that by controlling the molecular beam energy (E_k) one can activate different adsorption pathways for molecules on surfaces. However, the effect of collimated and energy-selected beams impacting the surface at different incident angles has not been observed *in-situ* at the local molecular level until now. We will show high-resolution spatial images of the initial stages of oxygen adsorption on Si(111)-7x7 at different beam energies. The comparison of Si(111)-7x7 oxidation *via* thermal oxygen versus the specific adsorption sites that arise at different beam energies will also be discussed. The results indicate that using supersonic beams in this matter may provide enhanced control of semiconductor oxidation chemistry.

5:00pm **SS+AS+EM+EN-ThA9 Surface Band-Bending Upon Oxidation of Wurtzite and Zincblende InAs Depending on Surface Orientation and atomic Structure**, ***Rainer Timm**, M. Hjort, J. Knutsson, O. Persson, A. Troian, S. Lehmann, K.A. Dick, A. Mikkelsen*, Lund University, Sweden

InAs is known to typically show n-type behavior with an electron accumulation layer at the surface. Many studies have been performed for evaluating to which extend this behavior is due to adsorbates such as a native oxide layer, or to specific surface orientations and reconstructions of clean InAs. InAs nanowires (NWs) add an extra degree of complexity, since they can exist both in zincblende and wurtzite crystal structure, typically exhibiting unintended switching between both stacking orders during epitaxial growth. During recent years, a strong debate has been going on about how far such crystal phase mixing influences the conductivity of InAs NWs and therewith their suitability for high-mobility device application [1]. A staggered band alignment with band offsets in the range of up to 0.1 eV between zincblende and wurtzite conduction band edges has been reported, based on transport measurements in ambient atmosphere [2]. In contrast, our recent study of clean and unreconstructed InAs NW surfaces based on scanning tunneling microscopy and spectroscopy (STM/S) in ultrahigh vacuum showed aligned conduction band edges for zincblende [110[and wurtzite [11-20[surfaces [3].

Here, we present a systematic study of surface band-bending upon cleaning and oxidation of various InAs surfaces, including purely zincblende or purely wurtzite NWs, obtained by synchrotron-based X-ray photoemission spectroscopy (XPS). We were able to clean all investigated InAs surfaces from their native oxide by annealing them in the presence of atomic hydrogen [3]. Different rates of cleaning and re-oxidation were observed for the different surfaces. Even more importantly, from the energy shifts of the investigated core-levels upon oxidation, varying between 0.1 and 0.3 eV for various surfaces, we obtained significant differences in oxide-induced surface band-bending for different surface orientations. We will compare our XPS results with the atomic and local electronic structure of the specific surfaces as obtained by STM/S [4]. Our results indicate that the band alignment along InAs heterostructures, and therewith the transport properties of InAs NWs, depend on the surface orientation, composition, and atomic structure rather than the crystal phase of the specific InAs segments.

[1] Thelander *et al.*, Nano Lett. **11**, 2424 (2011)

[2] Dayeh *et al.*, Adv. Funct. Mater. **19**, 2102 (2009)

[3] Hjort *et al.,* ACS Nano **12**, 12346 (2014)

[4] Knutsson *et al.*, ACS Appl. Mater. Interfaces **7**, 5748 (2015)

5:20pm **SS+AS+EM+EN-ThA10 Control of Oxygen Defect Surface Injection in ZnO via Sub-Monolayer Sulfur Adsorption**, ***Ming Li**, E. Seebauer*, University of Illinois at Urbana-Champaign

Native oxygen defects within metal oxide semiconductors such as ZnO affect the material's performance in applications for photovoltaics, nanoelectronics, gas sensing, and photocatalysis. Previous work in this laboratory has shown that the semiconducting metal oxides surfaces can be used to manipulate the concentrations and spatial distributions of bulk oxygen defects, particularly oxygen vacancies. The interaction chemistry between bulk point defects and reactive sites on semiconductor surfaces is comparable in richness to the reactions of surfaces with gases. The present work discusses a novel mechanism of controlling oxygen defect injection in c-plane ZnO(0001) through surface active sites blocking with sub-monolayer sulfur adsorption. Oxygen diffusion rates were measured by exposing single-crystal ZnO to isotopically labeled oxygen ($^{18}O_2$) gas. Sulfur was deposited controllably via an electrochemical cell and characterized *in situ* by Auger Electron Spectroscopy (AES). The resulting diffusion profiles were measured by secondary ion mass spectrometry (SIMS). Kinetic parameters were extracted by fitting the diffusion profiles with a previously derived mass transport model. The preliminary data shows that sulfur adsorption decreases the oxygen defect injection rate by roughly three times through affecting the injection flux, which points to a site blocking model. Subsequent temperature and pressure dependence study will help us gain insights into detailed injection kinetic pathways.

5:40pm **SS+AS+EM+EN-ThA11 Investigation of the Role of Electronic Defects and Grain Boundaries in Sputter Deposited CdS/CdTe Junctions and Solar Cells**, ***Mohit Tuteja**,* University of Illinois at Urbana Champaign*, P. Koirala,* University of Toledo*, J. Soares,* University of Illinois at Urbana Champaign*, R. Collins,* University of Toledo*, A. Rockett*, University of Illinois at Urbana Champaign

Device quality CdS/CdTe heterostructures and completed solar cells (~12% efficient) have been studied using low-temperature photoluminescence (PL) as a function of temperature (82-295 K) and laser excitation power (0.02-2 mW). The CdS/CdTe junctions were grown on transparent conducting oxide covered soda lime glass using rf-sputter deposition. It was found that the luminescence shifts from being dominated by sub-gap defect-mediated emission at lower excitation powers to near band edge excitonic emission at higher excitation powers. The effect of copper (Cu) used in making back contacts was studied in connection with the CdS/CdTe junction PL. It was found that the presence of Cu suppresses the sub-band gap PL emissions. This effect was concluded to be due either to Cu occupying cadmium vacancies (V_{Cd}) or forming acceptor complexes with them. This points to a potential role of Cu in plugging sub-band gap recombination routes and hence increasing charge separation ability of the device. An energy band diagram is presented indicating various observed transitions and their possible origins.

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 $I \alpha (T_c - T)^{1/2}$. 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 ρ(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 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 μC/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

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*** TFD James Harper Award Finalist**

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 Si$_{1-x}$Ge$_x$/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 Al$_2$O$_3$ 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$_2$O$_3$ -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$_2$O$_3$ single layer is porous with a mean pore (spherical shape) radius of 7.2 nm while there are no pores in the second Al$_2$O$_3$ single layer. This agrees well with the SXRR showing a lower density of the first Al$_2$O$_3$ single layer (2.93 g/cm^3) than that of the second Al$_2$O$_3$ 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$_y$Ga$_{1-y}$ (78≤y≤85 at%) and Ni$_x$Fe$_{1-x}$ (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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Thin Film
Room: 114 - Session TF+PS-ThA

Thin Film Permeation Barriers and Membranes
Moderator: Mariadriana Creatore, Eindhoven University of Technology, Netherlands

2:20pm **TF+PS-ThA1 Synthesis, Characterisation and Engineering of Moisture Barrier Films Deposited in a Roll-to-Roll High Current Dielectric Barrier Discharge**, ***Hindrik de Vries***, FOM institute DIFFER, Netherlands **INVITED**

Atmospheric pressure plasma enhanced chemical vapor deposition (AP-PECVD) is a new and rapidly evolving technology having clear benefits in terms of equipment costs, footprint size and possibilities for in-line processing. The excellent scalability of the dielectric barrier discharge combined with the possibility to generate non-thermal plasma in low-cost helium free gas mixtures, are essential requirements for large scale processing of functional films on web-rolled substrates.

In this work a cylindrical drum shaped DBD reactor configuration was implemented to facilitate roll-to-roll processing. We performed a systematic study of the discharge physics investigated by fast ICCD camera and voltage-current waveforms and we comprehensively analyzed the silica-like films deposited under barrier deposition conditions using AFM, XPS, SE and FTIR.

The time evolution of the atmospheric discharge was studied in 2 orthogonal directions of the cylindrical electrode geometry showing a glow-like discharge character. Detailed AFM morphology study and surface statistical analysis of the silica growth dynamics was carried out. The microstructure of the silica layers was studied using polarized ATR-FTIR and linked to the water vapor transmission rate (WVTR). The remarkable power law scaling between WVTR and film thickness was tentatively explained by the percolating nature of the moisture transport through the films. Based on this hypothesis, different approaches were investigated towards (bi-)layer architectures using AP-PECVD as well as other deposition techniques. Such a bi-layer architecture typically consists of a first porous silica layers that is subsequently covered by a dense silica capping layer.

In this contribution we will focus on the processing of silica bi-layers synthesized in different deposition regimes. The process conditions of the layers will be discussed in the frame of different scaling parameters like the energy spent per precursor molecule and the local deposition rate. Gas permeation properties were characterized by Technolox Deltaperm and calcium test. It was shown that AP-PECVD grown silica thin films of less than 30 nm deposited on a porous silica layer can yield excellent overall moisture barrier values (WVTR) typically ~$6*10^{-4}$ g/m^2 day at 40ºC, 90%RH accelerated ageing conditions.

3:00pm **TF+PS-ThA3 Investigation on Nano-Porosity in Moisture Permeation Barrier Layers by Electrochemical Impedance Spectroscopy**, ***Alberto Perrotta,*** Eindhoven University of Technology, Netherlands, *S.J. Garcia Espallargas,* Delft University of Technology, Netherlands, *J.J. Michels,* Max Planck Institute for Polymer Research, Germany, *M. Creatore*, Eindhoven University of Technology, Netherlands

High-tech devices relying on organic semiconductors require device encapsulation against moisture and oxygen permeation, which would otherwise negatively affect the device opto-electrical performance.

The water permeation in inorganic moisture barriers has been shown to occur through macro-scale defects/pinholes (ranging from tens of nms to several μms) and nano-pores, down to sizes approaching the water kinetic diameter (0.27 nm). Both permeation paths can be identified by the calcium test, which allows discerning between the effective water vapor transmission rate (WVTR) and the intrinsic WVTR, the latter solely attributed to the permeation through the nano-porosity characterizing the bulk of the barrier layer. Recently [1], we have shown that ellipsometric porosimetry (EP) is a valid method to classify and quantify the nano-porosity content of inorganic barriers and a correlation has been found between their relative pore content and intrinsic WVTR values [1]. However, no information can be retrieved on the macro-scale defects nor on the kinetics of water permeation through the barrier, both essential elements in assessing the quality of the barrier layer.

In this study, electrochemical impedance spectroscopy (EIS) is demonstrated as a sensitive method to obtain quantitative information on both nano-porosity and macro-scale defects, complementing the barrier property characterization obtained by means of EP and calcium test.

EIS analysis is carried out on thin SiO_2 barrier layers deposited by plasma enhanced-CVD. The layer capacitance has been determined by modelling the impedance data with the proper equivalent circuit and the change of the capacitance upon water permeation has been followed. The Brasher-Kingsbury equation has been successfully applied and water uptake in the range of 0.8-4% have been found, in agreement with the nano-porosity content inferred by EP. A good linear correlation between the nano-porosity and the values of the electrical components used in the fitting procedure of the EIS data has been obtained, suggesting the direct calculation of open nano-porosity from an EIS fit. Furthermore, the kinetics of water permeation can be followed by EIS: the water diffusivity for the SiO_2 layers has been determined and found in agreement with literature values. Moreover, differently from ellipsometry-based techniques, EIS data are shown to be sensitive to the presence of local macro-defects, inferring its possible use for the prediction of the barrier performance with the calcium test.

[1] A. Perrotta *et al.*, Microporous Mesoporous Mat., 188 (2014) 163-171

4:00pm **TF+PS-ThA6 Thin-film Dielectrics for Chronic Nonhermetic Encapsulation of Electrically Active Neural Implants**, ***Stuart Cogan***, The University of Texas at Dallas **INVITED**

The needs of emerging clinical applications of neural stimulation and recording in the treatment of many diseases and disorders are driving a reduction in the size of implanted devices and the development of strategies to manage the large number of electrical interconnects between implanted electrodes and control electronics. The requirements for large numbers of electrodes, exceeding many hundreds for vision prostheses, and the ability to interface with nerves that may be as small as 100 microns in diameter, precludes the use of conventional packaging with hermetically sealed metal or ceramic cans. One of the few practical alternatives to hermetically sealed enclosures is the use of thin-film dielectrics, possibly combined with polymer over-layers. Besides the need for these thin-film coatings to provide effective passivation against corrosion, they also serve a multifunctional role providing adhesion between polymer and metal layers in flexible devices, providing a biocompatible interface to neural tissue and in some devices, providing a surface for functionalization with bioactive molecules. Conventional passivation materials such as silicon dioxide and silicon nitride are prone to corrosion *in vivo* and recent experience with polymer encapsulation such as Parylene-C suggests that this otherwise excellent barrier layer may fail after chronic implantation for more than about one year. The implanted electronics on these devices operates typically at 3 V or higher and neural stimulation involves pulsatile currents that may also induce unexpected failures at interfaces. In this context, other thin-film materials such as amorphous silicon carbide (a-SiC), ultra-nanocrystalline diamond (UNCD), and atomic-layer-deposition (ALD) Al_2O_3 are being investigated as alternative passivation materials that can provide chronic protection of active implants. A discussion of the physical and chemical requirements for these materials and results reported to date is presented. Emphasis is placed on understanding the constraints of the application including processing compatibility with temperature-sensitive substrates, the need for conformal coatings, and appropriate test methodologies to validate predictions of chronic *in vivo* lifetimes. Early results are promising with some combinations of thin-film and polymer encapsulation exhibiting excellent stability and biocompatibility. Of particular interest, are the relative roles and importance of interfacial properties and bulk barrier properties in achieve long-term chronic passivation of implanted active devices.

4:40pm **TF+PS-ThA8 Atmospheric Pressure Roll-to-Roll Plasma Enhanced CVD of High Quality Silica-like Bi-layer Moisture Barrier Films: The Influence of Input Energy**, ***Fiona Elam***, FUJIFILM Manufacturing Europe B.V., Netherlands, *A. Meshkova, S.A. Starostin,* DIFFER, Netherlands, *J.B. Bouwstra,* FUJIFILM Manufacturing Europe B.V., Netherlands, *M.C.M. van de Sanden, H.W. de Vries*, DIFFER, Netherlands

Atmospheric Pressure-Plasma Enhanced Chemical Vapour Deposition (AP-PECVD) is a new enabling technology that can be easily integrated into many existing manufacturing systems to facilitate the mass production of functional films. To date, roll-to-roll AP-PECVD has been successfully used to produce ultra-smooth, dense, 100 nm single layer silica-like thin films that demonstrate good water vapour barrier performance, therefore showing particular promise as a technique in the field of protective layer synthesis for flexible organic solar cells. However, this technology is only viable for moisture barrier production if high quality films can be manufactured at high throughput and at low cost. The generation of bi-layer silica-like thin films comprising a 'dense layer' synthesised using very low precursor gas flows deposited on top of a 'porous layer' synthesised at a high deposition rate, could provide one potential solution to this scientific challenge.

A glow-like AP dielectric barrier discharge in a roll-to-roll set-up was used to deposit a series of ~90 nm bi-layer silica-like thin films composed of a ~60 nm 'porous layer' and ~30 nm 'dense layer' onto a polyethylene 2,6 naphthalate substrate by means of AP-PECVD. Tetraethyl orthosilicate (TEOS) was used as the precursor gas, together with a mixture of nitrogen, oxygen and argon. In each case, the deposition conditions for the 'porous layer' were kept constant, while the conditions for the synthesis of the 'dense layer' were varied in order to study the effect of increased input energy per precursor gas molecule (~6 – 70 keV/TEOS molecule) on the chemical composition and porosity of the 'dense layer' and hence, the influence of this 30 nm layer on the moisture barrier performance of the overall film.

Each film was characterised in terms of its water vapour transmission rate, its chemical composition (*s*-, *p*- and *un*-polarised Attenuated Total Reflectance-Fourier Transform Infrared spectroscopy and X-ray Photoelectron Spectroscopy) and its morphology (Atomic Force Microscopy) as a function of the input energy per precursor gas molecule during the 'dense layer' deposition. The analysis provided valuable information concerning the structure of the silica network within each 'dense layer', and hence the influence of input energy per precursor gas molecule on the ultimate film quality.

The ~90 nm bi-layer silica-like thin films were seen to exhibit water vapour transmission rates of at least 6.2×10^{-4} g m^{-2} day^{-1} (at 40°C, 90% RH), illustrating that it is possible to produce exceptionally high quality moisture barrier films using the presented bi-layer approach in a roll-to-roll AP-PECVD set-up.

5:00pm **TF+PS-ThA9 Use of Aluminum Oxide as a Permeation Barrier for Producing Thin Films on Aluminum Substrates**, ***James Provo***, Consultant, J. L. Provo Consulting

Aluminum has desirable thermal properties (i.e. conductivity, diffusivity and specific heat), electrical and optical properties of resistivity and reflectivity, and the characteristic of being non-magnetic and having a low atomic weight (26.98 g-atoms), but because of its low melting point (660°C) and ability as a reactive metal to alloy with most metals, it has been ignored as a substrate for use in processing thin films. The author, proposed a simple solution to this problem, by putting a permeation barrier of (Al_2O_3) onto the surface of Al substrates, by using a standard oxidation process of the surface (i.e., anodization), before additional film deposition of reactive metals at temperatures up to 500°C for 1 hour, without the formation of alloys or inter-metallic compounds that would affect the properties of the Al substrates. The chromic acid anodization used (MIL-A-8625) produced a film barrier of ~ 10k Å of alumina. The fact that refractory Al_2O_3 can inhibit the reaction of metals with Al at temperatures below 500°C suggests that Al is a satisfactory substrate if properly oxidized prior to film deposition. To prove this concept, thin film samples of Cr, Mo, Er, Sc, Ti, and Zr were prepared on anodized Al substrates and studied by Auger/ argon sputter surface analysis to determine any film substrate interactions. In addition, a thin film of (ErD_2) on an anodized aluminum substrate was studied with and without the alumina permeation barrier. Films for study were prepared on 1.27 cm O.D. high purity Al substrates with ~ 5k Å of the metals studied after anodization. Substrates were weighed, cleaned, and vacuum fired at 500°C prior to use. The aluminum substrates were deposited with the metals studied, using standard electron beam evaporation techniques, and after film deposition the erbium film was hydride with D_2 gas using a standard air-exposure hydriding technique. All processing was conducted in an all metal ion pumped high vacuum system. Results showed that e-beam deposition of all films studied onto Al substrates could be successfully performed, if a permeation barrier of Al_2O_3 from (5-10)k Å was made prior to thin film deposition up to temperatures of 500°C for 1 hour. Dihydrides, can also be successfully produced with full gas/metal atomic ratios of ~ 2.0 as evidenced by the (ErD_2) thin films produced. Thus the use of a simple permeation barrier of Al_2O_3 on Al substrates prior to additional metal film deposition, was proven to be a successful method of producing both thin metal and hydride films of various types for many applications without the formation of alloys or inter-metallic compounds that would affect substrate properties.

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:

1. Xin-Z. Liu, Zhijiang Ye, Yalin Dong, Philip Egberts, Robert W. Carpick, and Ashlie Martini. Dynamics of Atomic Stick-Slip Friction Examined with

Atomic Force Microscopy and Atomistic Simulations at Overlapping Speeds, *Phys. Rev. Lett.***114**, 146102 (2015).

2. Qunyang Li, Yalin Dong, Danny Perez, Ashlie Martini, and Robert W. Carpick. Speed dependence of atomic stick-slip friction in optimally matched experiments and molecular dynamics simulations. *Physical Rev. Lett.* **106**, 126101 (2011).

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]** .

References:

[1] R. Pawlak, S. Kawai, T. Glatzel, E. Meyer. *Single Molecule Force Spectroscopy* (ncAFM, *vol.3*, Springer, Japan 2015).

[2] S. Kawai et al., Quantifying the atomic-level mechanics of single long physisorbed molecular chains, *Proc. Nat. Acad. Sci.*, **111**, 3968–3972 (2014)

[3] R. Pawlak *et al* . *Intramolecular response of a single porphyrin molecule during AFM manipulations.* Submitted.

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.

Thursday Evening Poster Sessions

2D Materials Focus Topic
Room: Hall 3 - Session 2D-ThP

2D Materials Focus Topic Poster Session

2D-ThP1 Spin-Orbit Coupling in the Band Structure of Monolayer WSe_2(0001), ***Iori Tanabe***, University of Nebraska - Lincoln, *D. Le*, University of Central Florida, *A.V. Barinov*, Sincrotrone Trieste, Italy, *E. Preciado, M. Isarraraz*, University of California - Riverside, *T. Komesu*, University of Nebraska - Lincoln, *L. Bartels*, University of California - Riverside, *T.S. Rahman*, University of Central Florida, *P.A. Dowben*, University of Nebraska - Lincoln

WSe_2 and the related metal dichalcogenides MX_2 (with M = V, Mo, W, Ta and X = S, Se, Te) are layered structures that in each plane consist of a hexagonal honeycomb lattice reminiscent of graphene or graphite. WSe_2 is a semiconductor, rather than a gapless semiconductor (like graphene) or semimetal, and is expected to have applications for new spintronic devices where spin-orbit coupling might play a valuable role. Here, we used high-resolution angle resolved photoemission spectroscopy (ARPES) and inverse photoemission spectroscopy (IPES) to map out the electronic band structure of single-layer WSe_2. The splitting of the top of the valence band due to spin-orbit coupling was found to be 513±10 meV, far larger than that for MoS_2. As expected the top of the valence band is at $\underline{K}$. Overall, density functional theory (DFT) calculations were in excellent agreement with the ARPES results, and we have verified that the few discrepancies between theory and experiment were not due to the effect of strain. Cobalt on WSe2 is seen to have a very complex interface, with strong interactions, as seen in the changes to the experimental electronic structure. Without the complexity of a metal adlayer, WSe_2 is seen to be routinely Se rich and should thus be reliably p-type.

2D-ThP2 Ferroelectric Control of Monolayer MoS_2 via Direct Single-Layer Growth on $LiNbO_3$, ***Ariana Nguyen***, *E. Preciado, V. Klee, D. Sun, I. Lu, D. Barroso, L. Bartels*, UC Riverside

We present the direct chemical vapor deposition (CVD) growth of monolayer molybdenum disulfide (MoS_2) onto periodically poled lithium niobate. Single-layer MoS_2 displays a preference for the ferroelectric domains polarized “up” with respect to the surface. This may offer the possibilities of templated growth of TMD films using the substrate ferroelectric polarization as a pattern. Piezoresponse force microscopy reveals that the MoS_2 film maintains the substrate polarization on the “up” domains while partially quenching it on the “down” domains. Electrical transport measurements suggest the ability to invert the single-layer CVD MoS_2 majority charge carrier via gating depending on the domain orientation of the periodically poled lithium niobate substrate.

2D-ThP4 Thermally Conductive Graphene-Polymer Composites, ***Michael Shtein***, *O. Regev*, Ben Gurion University, Israel

The rapidly increasing device densities in electronics dictate the need for efficient thermal management. If successfully exploited, graphene, which possesses extraordinary thermal properties, can be commercially utilized in polymer composites with ultrahigh thermal conductivity (TC). The total potential of graphene to enhance TC, however, is restricted by the large interfacial thermal resistance between the polymer mediated graphene boundaries. We report a facile and scalable dispersion of commercially available graphene nano platelets (GnPs) in a polymer matrix, which formed composite with an ultra-high TC of 12.4 W/mK (vs. 0.2 W/mK for neat polymer).[1] This ultra-high TC was achieved by applying high compression forces during the dispersion resulting in gap closure between adjacent GnPs with large lateral dimensions and low defect densities. We also found strong evidences for the existence of a *thermal percolation threshold*. Finally, the addition of electrically insulating nano-boron nitride to the thermally conductive GnP-polymer composite significantly reduces its electrical conductivity (to avoid short circuit) and synergistically increases the TC. The efficient dispersion of commercially available GnPs in polymer matrix provides an ideal framework for substantial progress toward large-scale production and commercialization of GnP-based thermally conductive composites.

Reference: Shtein M., Nadiv R., Buzaglo M., Kahil K. and Regev O., Thermally conductive graphene-polymer composites: size, percolation and synergy effects, *Chemistry of Materials*, 2015, 27, 2100–2106 .

2D-ThP5 Low Temperature Raman and Photoluminescence Measurements of MoS_2 Layer Grown by Chemical Vapor Deposition, ***Barbara Nichols***, U.S. Army Research Laboratory, *R. Ghosh, S.K. Banerjee*, University of Texas at Austin

The temperature-dependent Raman spectroscopy and photoluminescence mapping measurements of molybdenum disulfide (MoS_2) layers grown on silicon oxide (SiO_2) by chemical vapor deposition were performed. As grown, the MoS_2 monolayers are shaped as either hexagons or triangles with smaller dendritic adlayers randomly distributed throughout the layer. Specifically, Raman and PL mapping of a 20 micron wide hexagon was performed at room temperature in air and in vacuum. In both air and vacuum, the Raman A_{1g} – E_{2g} separation was wider for the dendritic adlayers than for the monolayer MoS_2 as well as a decreased PL intensity was observed for the dendrites when compared to the monolayer. Raman and PL mapping of the MoS_2 hexagon revealed these trends remained as the temperature was decreased from room temperature to 4 K. At 4 K, differences between the dendrites and the monolayer MoS_2 were mainly observed by the PL measurements. PL peak position shifts as much as 15 meV and peak shapes were observed for the A and B exciton transitions.

2D-ThP6 CVD Growth of Single-Layer TMD Films Onto Pre-Fabricated Substrate Structures, *B. Davis, E. Preciado, V. Klee, A. Nguyen, I. Lu, D. Barroso, S. Naghibi, I. Liao, G. von Son, D. Martinez-Ta*, ***Ludwig Bartels***, UC Riverside

We demonstrate the growth of transition metal dichalcogenides (TMD) single-layer films through chemical vapor deposition (CVD) onto pre-fabricated patterns on SiO_2/Si surfaces. For an ultimate technological application of single-layer TMD films, they need to be integrated into lithographic structures on SiO_2/Si substrates; exfoliation and/or transfer are not suitable or scalable techniques. The comparatively low growth temperatures of TMD films (about 700°C) compared to graphene (about 1000°C) is a crucial advantage of the former, as SiO_2/Si features can sustain the growth temperature. Here we offer examples of how pre-fabricated patterns can control the growth of TMD films, and how the latter arrange themselves into former to offer features (e.g., natively suspended material) that is typically not available directly from growth onto conventional flat substrates. We explore the electrical and optical properties of single-layer growth on substrates with holes, pillars, and trenches.

2D-ThP7 MoS_2 Thin Films Deposited by Chemical Bath Deposition on Si and Glass Substrates, *D.E. Perez-Barragan*, Escuela Superior de Ingenieria Quimica e Industrias Extractivas-IPN, Mexico, *A. Garcia-Sotelo, E. Campos*, Cinvestav-IPN, Mexico, ***Orlando Zelaya-Angel***, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, *M. Melendez-Lira*, Cinvestav-IPN, Mexico

Even when the increasing interest in MoS_2 is driven by their properties as a 2D material, the deposit of MoS_2 films using low cost techniques is interesting and allows to explore the feasibility to find routes to produce low cost materials capable to improve photovoltaic structures, etc. The results of the deposit by chemical bath deposition of MoS_2 films employing Si and glass substrates are presented. Two precursor were employed: Ammonium molybdate $(NH_4)2MoO_4$ and Ammonium molybdate tetrahydrate $(NH_4)6Mo_7O_{24} \cdot 4H_2O$. It was found that the first precursor is adequate to obtain amorphous MoS_2 films on glass while the second allows to obtain amorphous films on silicon.

The samples crystallized after a thermal annealing process carried out at 300 °C. UV-Vis spectroscopy indicated a blue-shift in the absorption edge from the MoS_2 bulk value, probably related to the film thickness. Samples were characterized also by XPS, Raman and AFM. The results are discussed in terms of the structural characteristic of the films and the interaction with the substrate.

*: Partially funded by CONACyT-Mexico

2D-ThP8 Development of Arrays of Field Effect Transistors Based on CVD Graphene and TaN as Metal Electrode, ***Aline Pascon***, UNICAMP, Brazil, *C.C. Silva*, University of Campinas, Brazil, *J.F. Souza*, UNICAMP, Brazil, *L.T. Kubota*, University of Campinas, Brazil, *L.R.C. Fonseca, J.A. Diniz*, UNICAMP, Brazil

Since graphene was successful isolated for the first time by microcleaving of graphite [1], this material has attracting a significant attention of all scientific community, mainly due to its outstanding electronic properties, making it an ideal material to replace the silicon in the traditional FETs. However, the implementation of graphene in the development of FETs has two major issues that should be overcome. The first is that graphene obtained from microcleaving or exfoliation of graphite, does not feature like a scalability technique to be employed in the fabrication of arrays of FETs. The second issue is related with the high contact resistance that appears in the interface metal/graphene. In order to replace the silicon by the graphene as a channel material, a suitable contact with electrodes is required. Aiming to overcome the related issues, herein we have addressed the implementation into arrays of FETs by large area of monolayer graphene produced by the CVD process. Furthermore, we evaluated the effects of the replacement of the conventional, non-refractory metallic electrodes such as Ti/Au or Ti/Pd for the refractory metallic electrodes, such as tantalum nitride (TaN) that has a work function similar to graphene reducing the barrier between metal and graphene.

The CVD graphene was grown based on the procedure proposed by Ruoff and coworkers [2]. This graphene film was transferred on FETs where 22 nm TaO_x was used as gate dielectric, in just one step, homogenous and free from PMMA residues or other contamination. The Raman spectra obtained from different areas of the graphene displays a typical G peak at 1587 cm^{-1}, free of defects and a 2D peak at 2684 cm^{-1}, indicating a monolayer of graphene [3].

After the transferring process, the graphene was isolated between the source and drain TaN electrodes due to the photolithography step followed by the oxygen plasma etching, to remove the graphene in the outside area, creating a contact with the electrodes, similar to the dielectric gate. All this process was carried out directly on a die of 2.5 cm^2 containing four arrays with 300 FETs each. The latter two processes define the active region of the device, where the electronic transport will occur through the graphene monolayer.

Measurements of electrical properties, with transconductance of 3 mS and contact resistance of 3 kΩ indicate that our devices can achieve high performance, while allows fabricating a massive number of FET-Graphene devices through a simple, fast and scalable approach.

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2D-ThP11 Conductance-Based Structural Characterization of Hybrid, 2-Dimensional, Molecule-Nanoparticle Arrays, *Joshua Hihath, C.E. McCold, Q. Fu,* University of California, Davis, *J.Y. Howe*, Hitachi High-Technologies Corporation

Molecule-nanoparticle hybrid systems have emerged as promising materials for applications ranging from chemical sensing to nanoscale electronics. However, creating reproducible and repeatable 2-dimensional composite materials with precise electronic properties has remained an important challenge to the implementation of these meta-materials. Understanding the sources of variation that dominate the charge transport properties of these systems is essential for the advancement of nanoparticle-array based devices. In this work, we use a combination of charge-transport measurements, electron microscopy, optical characterization, and chemical ligand exchange to determine the role of morphology, structure, and array interconnection on the charge transport properties of 2-dimensional, monolayer arrays of molecularly-interlinked gold nanoparticles. Using these techniques we are able to determine the role of assembly-dependent, particle dependent, and molecule dependent defects on the conductivities of the monolayer films. These results demonstrate that micron-scale assembly processes dominate the dispersion of the conductance values, and result in order-of-magnitude differences in the conductance values, while nanoscale properties related to the nanoparticle and ligand features dictate the mean value of the conductance. By performing a systematic study of the conductance of these arrays as a function of nanoparticle size we are able to extract the carrier mobility for specific molecular ligands. We show that nanoparticle dispersion correlates with the void density in the array, and that because of this correlation it is possible to accurately determine the void density within the array directly from conductance measurements. These results demonstrate that conductance-based measurements can be used to accurately and non-destructively determine the morphological and structural properties of these hybrid arrays, and thus provide a characterization platform that helps move 2-dimensional nanoparticle arrays toward robust and reproducible electronic systems. Based upon this understanding, it is then possible to control the conductance values of the hybrid arrays by tuning both the distance between nanoparticles, and the conjugation of the molecules interlinking the nanoparticles. This control allows the conductance of the 2D films to be tuned over a range of ~7 orders of magnitude.

Additive Manufacturing/3D Printing Focus Topic
Room: Hall 3 - Session AM-ThP

Additive Manufacturing/3D Printing Poster Session

AM-ThP1 Anisotropic Evaluation of Mechanical Properties Related to Printing Direction and Development of Nanocomposite Materials to Establish Direct Digital Manufacturing, *Hiroaki Sakaguchi, A. Matsumuro, K. Takeda*, Aichi Institute of Technology, Japan

3D printing technique is strongly leading the next industrial revolution in all over fields. The manufacturing methods are used by additive processes using successive layers of a lot of kind of materials. In the past few years, the rapid development of 3D technologies has changed from data visualization models and so on to the manufacturing of industrial production including mass-production (DDM). Many difficult problems should be overcome in order to establish DDM technology as the general industrial products manufacture method. One of the representative problems is the durability or strength of the products. 3D printing systems deposits melt or soften materials in a layer state on solid parts. Layered structures are formed in the whole products, and extreme low strength interfaces are fabricated at the same time. It is necessary to optimize a printing direction according to the load that determines the strength and durability of the product as one of manufacturing process.

Our study investigated an optimal molding direction procedure with respect to mechanical properties. Tensile and three points bending tests were done for standard plate type specimen made of polymer (ABS-like, Strasys Co., Ltd) using Ink-Jet-Type 3D printer (Connex500). We made three types of specimens, which were varied in the printing direction, respectively. These experiments mean that the effect of directions of layers entering in the molds on important mechanical properties. Three type specimens for tensile direction were molded as follows: (S1) plane molding with printing layers parallel to tensile direction, (S2) plane molding with vertical layers to tensile direction and, (S3) vertical molding with vertical layers to tensile direction. Experimental results of tensile strength, Young's modulus and rupture stress of each specimen showed remarkable differences. The detail results were as follows: tensile strength of (S1) 50 MPa, (S2) 39 MPa, (S3) 35 MPa, Young's modulus of (S1) 1.1 GPa, (S2) 0.8 GPa, (S3) 0.7 GPa and rupture stress of (S1) 59 MPa, (S2) 46 MPa, (S3) 37 MPa. Bending test results showed the similar tendency of those of Young's modulus. These results became clear strongly significant specific anisotropy of mechanical properties related to printing directions. Therefore, establishment of DDM needs the logical molding process and construction of the database of mechanical properties of individual materials. Furthermore, another important problem concerning DDM must be development of new materials with strength enough for practical use. Now we have studied new nanocomposite materials with innovative high strength. We will present the results at the conference.

AM-ThP2 A New Technique to Make an Insulating AlN Thin Film to be Conductive by Spontaneous via Holes formed by MOCVD and its Application to realize Vertical UV LED on n^+Si Substrate, *Noriko Kurose, Y. Aoyagi*, Ritsumeikan University, Japan

A new Technique to make an insulating AlN thin film to be conductive by spontaneous via holes formed by MOCVD and its application to realize vertical UV LED on n^+Si substrate

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Abstract

For growing AlGaN epitaxial layer on Si substrate, AlN buffer layer between Si substrate and AlGaN epitaxial layer is indispensable to avoid Si melt-back phenomena coming from direct contact of AlGaN to Si substrate. However, AlN is insulating material even though highly doped. To fabricate vertical type device like vertical UV LED and vertical UV light sensor, the conductive n-AlN is indispensable to insure direct current flow from p-electrode to n-Si substrate. We have succeeded in developing a new technique to grow conductive n-AlN using spontaneous via holes in AlN buffer epitaxial layer grown on n+Si substrate using MOCVD and succeeded in fabricating and operating vertical UV-LED and vertical UV sensor using this technique.

Via holes in AlN buffer layer are spontaneously formed by introducing thin Al layer deposition on the Si substrate. This Al thin layer forms a mask to make spontaneous via holes. Formation of via holes are confirmed by AFM and EDX measurement. Via holes are filled by conductive n-AlGaN and the current flows through these via holes. This current flow through via holes is confirmed by EBIC measurement. The density and the size of via holes are controlled by changing the growth condition of MOCVD. The size of via holes can be varied from 0.1 to 2μm depending on the TMA feeding amount in an initial stage of Al thin layer formation. By growing the p-n junction on the layer with multi quantum wells we have succeeded in vertical LED fabrication (substrate removal free vertical LED, RefV-LED) and operation with direct current flow from p electrode to n$^+$Si substrate at the wavelength of 350-400nm with good I-L and I-V performance and near field pattern. The built in voltage of the p-n junction was 3.8V and the break down voltage was more than 35V. The built in voltage is almost same as the band gap of AlGaN used in this RefV-LED. The large breakdown voltage of this device shows us that good p-n junction is formed. Our device can be fabricated without any photoresist processes and is simple to fabricate. These results show us our techniques will open a new window to fabricate a new DUV LED and UV sensor as well.

AM-ThP3 Novel Deep Si Etching Process for Green IOT

Takahide Murayama, ULVAC Inc., Japan

TSV (Thru Silicon Via) application for 2.5D silicon interposers and 3D stacked devices is expected to realize a next-generation semiconductor device applied for upcoming IOT world with high packaging density, power saving, and high-speed signal transmission, etc. Generally, SF6 gas has been applied to form TSV in dry etching process because of its useful properties; reasonable cost, chemical safety, and dissociation property which generates a lot of fluorine radicals. Abundant fluorine radicals contribute to achieve higher silicon etching rate, but in the perspective of Global Warming Potential (GWP), SF6 has extremely high potential (GWP = 22200, 100 year base), gives a great impact to greenhouse effect. So, various gases have been offered to alternate SF6. In series SFx (x=0 to 6), there are limited species which have industrial stability, some of them characteristic properties in the points of low GWP and dissociation to generate fluorine radicals. SF4 gas has very low GWP in SFx series . Because SF4 immediately reacts with H2O in atmosphere, generates HF and SOx. GWP for HF and SOx have not been set due to their water-soluble property . In addition to low GWP property, the bond strength in SF4 has unique property. In SF6, SF5-F bond strength is 387 ± 13 kJ/mol. On the other hand, SF3-F bond strength in SF4 is 354 ± 13 kJ/mol . So, there is an expectation that SF4 can generate abundant fluorine radicals compared with SF6. From above properties, SF4 may be one of the SF6 alternative gases for TSV dry etching process.

AM-ThP4 High Resolution Two Photon and 3D Holographic Lithography Structure Production and Conversion to Higher Index Materials

Steven Kooi, MIT Institute for Soldier Nanotechnologies

3D structured polymeric materials are produced by multi-beam laser interference or two photon direct write lithography[1] using either a 355 nm pulsed Nd:YAG laser or a 780 nm Ti:Sapphire femtosecond laser. Samples are also constructed by combining the two techniques.

In order to obtain more interesting and measurable optical properties, the polymeric structures produced by holographic lithography and two-photon lithography are converted into higher index of refraction materials (Si and Ge) by atomic layer deposition, reactive ion etching and chemical vapor deposition techniques.

Optical properties of the photonic structures produced are calculated and measured by local reflectivity and transmission measurements as well as with near field scanning optical microscopy. The 3D structure quality and all steps of the transformation from polymeric to high index materials are also characterized by serial focused ion beam (FIB) milling and imaging.

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Applied Surface Science
Room: Hall 3 - Session AS-ThP

Applied Surface Science Poster Session

AS-ThP1 Applications of EMSL's Radiochemistry Annex (RadEMSL) in Understanding of the Chemical Fate and Transport of Radionuclides in Terrestrial and Subsurface Ecosystems

Mark Engelhard, Pacific Northwest National Laboratory

(RadEMSL) is a radiochemistry facility, which is part of EMSL, Environmental Molecular Sciences Laboratory, a Department of Energy Office of Science User Facility sponsored by the Office of Biological and Environmental Research and located at PNNL. This facility is designed to accelerate scientific discovery and deepen the understanding of the chemical fate and transport of radionuclides in terrestrial and subsurface ecosystems. In this poster we present results obtained from two different studies that have utilized the X-ray Photoelectron Spectroscopy (XPS) capability in this facility.

The first application involved XPS analysis of Uraninite (UO_2). UO_2 is the primary component of most nuclear fuels, and can be a major phase in bio-remediated uranium- contaminated soils and aquifers. Understanding the mechanisms of UO_2 surface oxidation and corrosion is essential to predicting its stability in the environment throughout the nuclear fuel cycle. XPS shows clear evidence of U(IV) and U(V) oxidation states consistent with computational results. This new mechanism may be relevant to other fluorite structures, including plutonium dioxide (PuO_2).

The second application involves XPS analysis of Np. Neptunium (Np) is a long-lived radionuclide environmental contaminant associated with weapons production and processing that is transported in the subsurface as actinyl NpO_2^+. The radioactive metallic element Np is created when uranium-based nuclear fuel is burned up in electricity-producing commercial reactors and in plutonium-producing reactors operated for military purposes. Researchers examined factors that impact structural incorporation of Np(V) neptunyl and U(VI) uranyl ions into carbonate and sulfate minerals. Co-precipitation of Np(V) into mineral structures could reduce transport in the subsurface and shows promise as a groundwater remediation strategy.

Rad(EMSL) offers experimental and computational tools uniquely suited for actinide chemistry studies. The spectroscopic and imaging instruments at this facility are ideally designed for the study of contaminated environmental materials, examination of radionuclide speciation and detection of chemical signatures. The annex houses nuclear magnetic resonance instruments and surface science capabilities, such as X-ray photoelectron spectroscopy, electron microscopy, electron microprobe, transmission electron microscopy and scanning electron microscopy.

AS-ThP2 XPS and AES Characterization of Tribofilm Formation on Non-Metallic Coatings Using ZDDP and Ionic Liquid Lubricant Additives

Harry Meyer III, *J. Qu, Z.B. Cai, C. Ma, H. Luo*, Oak Ridge National Laboratory

Interactions between oil additives and non-metallic surfaces are less well understood than tribofilm formation on metallic surfaces. The most common anti-wear additive for metallic surfaces is zinc dialkyldithiophosphate (ZDDP). In this study, ZDDP and a phosphonium–organophosphate ionic liquid (IL) are used with three hard coatings (AlMgB14– TiB2, TiB2, and diamond like carbon), to determine what, if any, tribofilms are formed when sliding against a steel ball. Systematic characterization was conducted on the coating wear scars including top surface morphology imaging and elemental mapping, layer-by-layer chemical analysis, and cross section nanostructural examination. For boride coatings, tribofilms formed by ZDDP+IL are up to 50-70 nm thick with 75-80% surface coverage. On the other hand, tribofilms on DLC were <25 nm thick and only covered 20-30% of the contact area. The presence of iron compounds in the tribofilms suggests a critical role for wear debris in tribofilm formation. In addition, oxidation products of TiB_2 were detected in the tribofilms. No involvement of the DLC surface in tribofilm formation was observed. Results suggest that wear debris digestion and contact surface reaction both are critical in tribofilm formation: the former process is responsible in forming the bulk of the tribofilm and the latter provides strong bonding of the tribofilm to the contact surface. In this poster, the emphasis will be how scanning Auger microanalysis and x-ray photoelectron spectroscopy were used for characterizing the ZDDP+IL-derived tribofilms.

AS-ThP3 XPS Sputter Depth Profiling of Organometallic Multilayer Materials using Massive Argon Cluster Ions

Simon Hutton, Kratos Analytical Limited, UK, *T. Bendikov,* Weizmann Institute of Science, Israel, *W. Boxford, S.C. Page, J.D.P. Counsell, A.J. Roberts, C.J. Blomfield, S.J. Coultas*, Kratos Analytical Limited, UK

Thin polymer films are found in an enormous range of devices and have many applications from use in semi-conductors, displays and solar cells to corrosion protection and packaging. New ion sources such as the multi-mode Ar gas cluster ion source (GCIS) have revolutionised the study of such organic thin films by depth profiling with techniques such as X-ray photoelectron spectroscopy (XPS). As reported elsewhere the chemical composition of organic thin films may now be determined as a function of depth by a combination of XPS analysis and etching using massive Ar ions.

In this study we present results from GCIS XPS depth profiling of multi-layer organometallic thin films. The films consist of two well defined and iso-structural osmium and ruthenium polypridyl complexes. These complexes are deposited from solution in a sequence-dependent assembly regime leading to self-propagating molecular assemblies with distinct internal interfaces and composition. [1] The layer-by-layer deposition approach used here allows multiple building blocks to be incorporated into the film.

Depth profiling through the films using the GCIS allowed the structure to be confirmed and relative layer thicknesses to be tentatively compared. The depth profiles were carried out using optimised conditions for cluster formation and X-ray exposure was limited to reduce detrimental effects, including modification of the etch rate, noted elsewhere. [2]

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AS-ThP4 XPS Analysis and Sample Preparation for EBSD Analysis using Argon Gas Clusters, ***Adam Bushell***, Thermo Fisher Scientific, UK, *R. Simpson,* University of Surrey, UK, *C.J. Stephens, C. Deeks, T.S. Nunney, J.P.W. Treacy*, Thermo Fisher Scientific, UK

The use of noble gas ions for sputter cleaning and profiling materials in X-ray Photoelectron Spectroscopy (XPS) analyses is well established. Monatomic ions are generally used while analysing hard inorganic materials, providing efficient cleaning and a good sputter rate while profiling. More recently, argon ion clusters have been found to be very effective at cleaning and profiling organic materials. Cluster ion sputtering of these materials is suitable for cleaning the surface without inducing chemical modification, but it also has potential for preparing surfaces for analysis by techniques other than XPS.

In this presentation we will show the results of an investigation into using a range of cluster energies and sizes not only for XPS, but how they can be used for sample preparation in EBSD. We will illustrate the potential level of successful EBSD analysis that can be achieved when the appropriate etching criteria are used on a sample.

AS-ThP5 Comprehensive Characterization High-k Dielectric Films Deposited by ALD using Multi-Technique Surface Analysis, ***Richard White***, Thermo Fisher Scientific, UK

It has been known for many years that XPS is the ideal technique for characterizing ultra thin layers encountered during semiconductor device fabrication. Standard XPS analysis allows the analyst to detect and quantify elements and chemical bonding states in the stack of layers within 5-10nm thickness. Extension of the analysis to angle resolved XPS (ARXPS) adds another dimension to the data, enabling non-destructive depth profiling of the stack and the measurement of buried layer thickness.

Modern XPS spectrometers, which also come pre-configured with additional surface analysis techniques, can measure several other parameters of interest to the semiconductor engineer/scientist. As well as measuring surface elemental and chemical state information, XPS can provide the analyst with electronic information such as band gap and valence band offset. The complementary technique of Reflection Electron Energy Loss Spectroscopy (REELS) can also give a measurement of band gap in those situations where XPS has trouble, e.g. when the stack contains hafnium oxide.

Finally, if an XPS spectrometer is also configured with Ion Scattering Spectroscopy (ISS) then a direct indication of film surface coverage can be made. This technique measures the kinetic energy of noble gas ions scattered from a surface and can be used to investigate the growth mode of high-k films during atomic layer deposition.

AS-ThP6 XPS and ToF-SIMS Characterization Functionalized 3D Mesostructures fabricated by Direct Laser Writing, ***Michael Bruns***, *A. Welle, A.S. Quick, T. Claus, G. Delaittre,* Karlsruhe Institute of Technology, Germany, *T.S. Nunney,* Thermo Fisher Scientific, UK, *M. Wegener, C. Barner-Kowollik*, Karlsruhe Institute of Technology, Germany

In recent years significant effort has been spent to develop strategies for the fabrication of structured (bio)polymer modified surfaces on various substrates to alter the properties or to introduce entities with specific functions. These still ongoing activities are mainly stimulated by the wide range of applications in various scientific fields, such as lab-on-a-chip technology, biointerfaces, and tissue engineering. The utilization of photo-triggered Diels-Alder reactions in combination with shadow masking is an established efficient tool to achieve precise chemically structured surfaces in 2D.[1, 2] However, when aiming at the fabrication of complex 3D structures equipped with different surface functionalities, direct laser writing (DLW) is the method of choice. Most recently developed photoresists comprising e.g. orthogonal thiol-yne chemistry and click chemistry for a subsequent dual surface modification open up a facile avenue to fabricate various structures with several tailored functionalities.[3] In all cases surface analytical methods are indispensable to prove the successful chemical modification in a non-destructive manner. Therefore, the present contribution focuses on the characterization of such 3D structures using the combination of X-ray photoelectron spectroscopy (XPS) and complementary time-of-flight secondary ion mass spectrometry (ToF-SIMS). For non-patterned samples XPS quantitatively evidences the successful functionalization of surfaces for every single reaction step, whereas ToF-SIMS allows for rapid investigation of the chemical 2D patterning at high spatial resolution. For selected samples advanced parallel XPS imaging is additionally applied to calibrate the ToF-SIMS findings, obtaining quantitative information. For the chemical surface characterization of the well-defined 3D structures, ToF-SIMS proves an efficient tool for non-destructive 3D characterization of excellent spatial resolution with the advantage to achieve chemical/molecular information simultaneously.

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AS-ThP7 Structure, Surface Analysis, Photoluminescent Properties and Decay Characteristics of Tb^{3+}-Eu^{3+} Co-Activated $Sr_2MgSi_2O_7$ Phosphor, *M.A. Tshabalala, O.M. Ntwaeaborwa,* University of the Free State, South Africa, ***Simon Dhlamini***, University of South Africa

Strontium magnesium silicate ($Sr_2MgSi_2O_7$) is an alkaline earth silicate that belongs to a group of natural minerals of the melilites group called sorosilicates. Sorosilicates have the same basic crystal structure and they can be represented by a general formula $A_2MT_2O_7$ (A = Ca, Sr, Na; M = Mg; and T = Si, Al, B)[1]. They usually crystalize in a tetragonal structure with a space group $P42_1m$. Due to their tetragonal crystal structure without an inversion center, lanthanides or transition metals can be incorporated easily as activators or dopants in melilite hosts[2]. Due to this ease of incorporation, melilites are today widely used as host lattices for rare-earth dopant and transitional metal ions to prepare light emitting materials or phosphors that can be used in many practical applications such as flat panel displays, light emitting diodes, solar cells and many other types of light emitting devices. In this study, we investigated the structure, chemical and electronic states, ionic and atomic distribution and photoluminescent properties of $Sr_2MgSi_2O_7$ single doped with Eu^{3+} or Tb^{3+} or co-doped with Eu^{3+} and Tb^{3+} by a solid-state reaction method. It turned out that the emission color could be tuned from blue to green or white depending on the dopant concentrations and the excitation wavelength.

The structure, stretching vibrations, chemical and electronic states, and photoluminescent properties were studied using X-ray powder diffraction (XRD), Fourier transformed infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), Time-of-flight secondary ion mass spectrometer (TOF-SIMS) and Photoluminescence (PL) spectroscopy respectively. The XRD pattern of the $Sr_2MgSi_2O_7$:Eu^{3+}, Tb^{3+} phosphor resemble the standard tetragonal phase of $Sr_2MgSi_2O_7$. The fitted XPS data demonstrated that there were two different Sr^{2+} sites in the host lattice and a site occupied by Mg^+ cations which connects the Sr^+ sites with the Si^+ ions. The TOF-SIMS results demonstrated localization and distribution of various ions within the host lattice (Sr_2MgSiO_7) including the Tb^{3+} and Eu^{3+} dopants. The photoluminescence data indicated that the emission colour could be tuned from blue-green depending on the concentration of Tb^{3+}. The white photoluminescence was observed from the Tb^{3+}-Eu^{3+} co-activated system. This tunable emission has potential application in solid state lighting like white and multicolor light emitting diodes (LEDs).

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AS-ThP8 XPS Study of Many-Electron Interaction & Exchange Interaction of Local Moments in Ion Beam Synthesized Ternary Transition Metal Silicides, ***Wickramaarachchige Lakshantha***, *M. Dhoubhadel, F. McDaniel, B. Rout*, University of North Texas

In recent years, the interest in ternary metal (iron) silicides system is triggered by its potential use in advanced silicon based opto-electronic devices. However the ternary silicides have been by far less studied than their binary counterparts despite the fact that they might be beneficial in decreasing the formation temperature of disilicides. The phase formation of ternary silicides is not well understood, because most often the ternary silicides are formed in metastable phases. Among the well-known synthesis techniques to form or modify the composition and physical properties of thin films, low energy ion implantation has shown to be a very powerful technique. The ternary metal silicides can be synthesized by sequentially implantation of two metals into a Si substrate. In this study, Fe-Co-Si & Fe-Ti-Si ternary phases were formed by sequentially implanting either Co or Ti, along with Fe into Si (100) at room temperature (RT). Dynamic ion implantation simulation was performed to determine the ion fluences for concentration saturation of implant ions in the Si matrix. Then the optimal saturation fluences of each ions were implanted at 50 keV into Si substrates. Further same implantation process were performed under an externally applied magnetic field. The samples were subsequently annealing at temperature ranging from 200 – 600 °C. X-ray diffraction (XRD) analysis shows that even without annealing significant amount of ternary phase formation for ion implantation under external magnetic field. Further structural evolutions of ternary phases were observed with the annealing temperature. X-ray photoelectron spectra show core-level (Fe 2p$_{3/2}$ & 3s) spectral asymmetry and splitting in these transition metal compounds. We believe this is the direct evidence of high Density of State (DOS) at valance band and a local moment in the ternary compounds.

AS-ThP9 Using ToF-SIMS to Characterize Surface Contamination in Sandia's Z Machine

James Ohlhausen, *B. Clark, R. Tang, D. Lamppa, D. Susan, R. Sorensen*, Sandia National Laboratories

The Z machine at Sandia National Laboratories is the world's most powerful and efficient laboratory X-ray radiation source. It generates 3-MV, 100-ns, 20-MA current pulses to compress target loads and produce high temperatures, high pressures, and 300-TW X-ray pulses for research in high energy density science. The Z machine target is fed by four parallel Magnetically-Insulated Transmission Lines (MITLs). The MITLs and target load hardware must be located in a high-vacuum chamber because of the exceptionally high electric- and magnetic-field stresses. The MITL electrode surfaces must be as clean as possible to maximize current delivery to the load. Residue from hardware handling, post-shot debris, and other environmental contaminants may generate electrode plasmas that contribute to current losses exceeding 6 MA for certain types of loads. Decreases in current delivery negatively affect all aspects of Z shot performance.

This analysis is part of a larger experiment to evaluate the efficacy of *in-situ* plasma cleaning within the Z machine's load region. Witness samples taken from different steps during hardware preparation and installation are used to characterize surface contaminants. ToF-SIMS is uniquely suited to perform analysis of these surfaces owing to its ability to image large areas while measuring elemental and chemical information. Both organic and inorganic species were detected in the form of particles and films. Contaminants found during the Z machine load hardware lifecycle were characterized before and after plasma cleaning to determine the effectiveness of plasma processing on the specific contaminants found. Methods of acquisition, analysis and quantification will be shown. Preliminary findings from the ToF-SIMS analysis will be presented.

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AS-ThP10 Going Beyond Visualization: Exploiting Synergies Between Electron Microscopy and ToF-SIMS

Kathryn Lloyd, *C.D. Chan, J.R. Marsh, D.J. Walls, S. Subramoney*, DuPont Corporate Center for Analytical Sciences

As is most often the case with research and development characterization challenges, no one analytical technique is able to "tell the complete story". The combination of inorganic and organic layers and components in today's advanced materials and display systems requires new sample preparation and analytical strategies. Natural systems such as leaves and seeds, as well as hair and skin, require molecularly specificity. A common analytical need is to be able to distinguish phases or layers at sub-micron lateral resolution, based on molecular signatures.

Electron microscopy (SEM or TEM) is often the first step towards sub-micron visualization. ToF-SIMS (secondary ion mass spectrometry) provides mass spectral data, and thus molecular specificity, with typically 1 micron lateral resolution. Since the lateral resolution of EDS, often used in conjunction with SEM to provide elemental maps, is also around 1 micron, the two techniques can be combined with the secondary electron images to provide a more complete chemical picture. Organic contamination in metal powder synthesis and feed granule coatings provide two examples.

Cross-sectional sample preparation using Focused Ion Beam (FIB) technology has allowed SEM and TEM visualization of layers and defects that could not be achieved using more traditional sample preparation approaches. A companion analysis for these types of samples is top-down ToF-SIMS depth profiling, as the depth resolution in this type of experiment is typically tens of nanometers or less. Combining the information from these two approaches is challenging and not always straightforward. Examples from displays and other layered structures will be shown.

AS-ThP11 The Benefits of Using All of the Measured Mass Channels During MVSA of ToF-SIMS Data Sets

Vincent Smentkowski, General Electric Global Research Center, *M.R. Keenan,* Independent Scientist, *H. Arlinghaus*, ION-TOF GmbH

Time of flight secondary ion mass spectrometry (ToF-SIMS) data sets are very large and contain a wealth of information about the material being analyzed. A typical image data set can be comprised of 256 x 256 pixels with a 0 to 900 amu (or greater) mass spectrum collected at high (M/ΔM ~10,000) mass resolution at every pixel. Data sets are often comprised of >1 x 10^{15} spectral channels. The challenge for a ToF-SIMS analyst is to scrutinize all of the measured information without bias in order to provide for the most robust understanding of the material being analyzed; this is especially important in an industrial setting where unknown samples are analyzed. Multivariate statistical analysis (MVSA) algorithms have assisted in ToF-SIMS data work up [1,2], however commercially available software is not able to handle data sets this large and the analysts often select mass intervals to utilize and/or degrades the mass resolution prior to MVSA analysis. In this poster, we will report first results obtained using MVSA software that is able to handle massive ToF-SIMS data sets. We demonstrate two important benefits of unbiased analysis of the massive ToF-SIMS data sets: (1) finding unexpected elements in real world samples (this is a reason why the authors never use peak lists for MVSA analysis) and (2) the ability to obtain high mass resolution results from data sets collected at nominal mass resolution (e.g., the beam alignment pulsing mode on ION-TOF instruments). The importance of these two benefits will be highlighted.

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AS-ThP12 Electron Gun Tilting and Shifting with O-Ring Stack System

In-Yong Park, *B. Cho,* KRISS, Korea, *C. Han,* KBSI, Korea, *D. Lee, S.J. Ahn*, KRISS, Korea

Most of the charged particle instruments (CPBIs) have the gun which generates a charge particle beam and column which controls a beam direction. In CPBIs, the precise alignment between gun and column is very important to get a best performance, such as high imaging resolution and patterning resolution. Generally, mechanical moving and electro-magnetic deflection are adopted to adjust beam path relatively in the each component. Most mechanical alignment operations use sliding single O-ring or thin metal bellows, which allow motion while preserving the internal vacuum. However, single O-ring allows the only small changes of shifting and tilting. For the double-deflector, an electronic part controlling the applied voltage or current is necessary, a fairly difficulty to assemble double-deflector part inside a vacuum chamber included. In this work, we center around on a simple and cheap electron gun alignment method in the laboratory experiment and early stages of CPBIs development.

To monitor the electron beam movement controlled by flange motion, we use a thermionic electron source and maintained a vacuum pressure of approximately 10^{-5} Pa with a combination of a rotary pump and a turbo-molecular pump which ran in tandem. In order to accelerate the generated electron beam, the electron gun system is floated at a negative 20 kV and the filament is heated by adjusting the current flow. Finally, the accelerated electrons hit the phosphor screen and make the visible light. We stacked ten O-rings and insert the metal center rings between O-rings to maintain the structure stably. We assembled four identical structures, all of which can shift the gun flange vertically and horizontally with clamping screws and separate it azimuthally with an equal space on the flange, which is under the O-rings. We monitored the beam position at the phosphor screen in real time shifting and tilting the flange on which electron gun is installed. Also, we get the nearly identical values comparing the experiment result and theoretical calculation result. This means that we can control the electron beam direction precisely with O-ring stack system maintaining the inside vacuum pressure steadily. We demonstrate a tilting angle of ±2.55° with shifts of ±2 mm experimentally[1], values which are generally sufficient for application to CPBI gun alignment, as this adjustable range can cover the error range when the parts are made and assembled. It can also be applied when insulation is needed between the flanges while maintaining some degree of freedom.

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AS-ThP13 Covalent Surface Modification of Silicon Oxide Substrate using Aliphatic Alcohols and Microwave Radiation, ***Austin Lee**, B.D. Gates*, Simon Fraser University, Canada

Microwave radiation is used to react alcohols with silicon oxide surfaces to form self-assembled monolayers (SAMs). Advantages of using alcohols as building blocks for the formation of SAMs include their widespread availability, ease of handling, and stability against side reactions. Challenges to preparing monolayers of aliphatic alcohols on silicon oxide surfaces include the relatively high temperatures and slow reaction kinetics of the alcohol condensation reaction. Microwave radiation delivers sufficient thermal energy for the condensation reaction to occur in a fast, efficient manner. To demonstrate this capability, monolayers of 1-butanol, 1-octanol, and 1-octadecanol were successfully formed with the assistance of a microwave oven, and the monolayers were evaluated using Soxhlet extraction, WCA, AFM, and XPS. We optimized this reaction to render the silicon oxide surfaces hydrophobic, and successfully coated alcohols onto both the native oxide of silicon substrates and glass microscope slides.

AS-ThP16 XPS Analysis of Polycrystalline Samples (Bi$_3$M)(Sb$_3$M)O$_{14}$ type Pyrochlore with M = Cu, Co and Zn, ***Lazaro Huerta**, R. Escamilla, M. Romero,* Universidad Nacional Autonoma de Mexico*, M. Flores,* Universidad de Guadalajara, Mexico*, A. Duran*, Universidad Nacional Autonoma de Mexico

The general formula of the oxide pyrochlores can be written as A$_2$B$_2$O$_6$O′ with four crystallographically nonequivalent atom sites. These compounds have potential applications in a variety of applications as catalysis, magnetic and ionic conducting materials. A particular pyrochlore-type phase with Bi$_{1.5}$ZnSb$_{1.5}$O$_7$ stoichiometry is used in ZnO-based varistors, a polyphasic ceramic with property based on the grain boundary phenomenon. Here, we synthetized the polycrystalline samples of (Bi$_3$M)(Sb$_3$M)O$_{14}$ with M = Cu, Co and Zn by solid state reaction. The samples were characterized by X-ray diffraction, Raman spectroscopy and X-ray photoelectron spectroscopy. X-ray diffraction studies revealed that the *a* lattice parameter increases with Cu, Co and Zn respectively. On the other hand, the Cu 2p, Co 2p, Zn 2p, Bi 4f and O1s core levels were analysed and the valence bands respective were studied.

AS-ThP17 XPS Analysis of CN$_x$ Thin Films, ***Niklas Hellgren**,* Messiah College*, R. Haasch,* University of Illinois at Urbana-Champaign*, S. Schmidt, L. Hultman,* Linköping University, Sweden*, I. Petrov*, University of Illinois at Urbana-Champaign

X-ray photoelectron spectroscopy (XPS) has for decades been one of the most widely used techniques for analyzing the quantity and bonding states of nitrogen in carbon-nitride compounds, in particular hard carbon-nitride films in wear-protective applications, and more recently for analyzing nitrogen doping states in graphene used for electronic applications. Interpretation of the C1s and N1s spectra, however, can be very challenging due to the many possible bonding configurations of N and C, combined with the inevitable interaction with oxygen and hydrogen on the film surface. A corresponding debate over interpretation has accompanied the field.

In this study we report on XPS studies of magnetron sputtered CN$_x$ thin films, with x ranging from ~0.1 to 0.6. Different growth conditions result in films of different structures, from amorphous to graphite-like and fullerene-like. In order to address some of the above-mentioned difficulties, films were analyzed by angular-resolved XPS, first *in-situ* in the growth and analysis chamber, then after air exposure, and finally after Ar ion etching using ion energies ranging from 500 eV to 4 keV.

The as-deposited films typically exhibit two strong N1s peaks at ~398-398.5eV (usually assigned to pyridine-like nitrogen, C–N=C), and ~400-400.7eV (graphitic nitrogen, –N<), with some nitrile contribution (–C≡N) in between, at ~399eV. Interestingly, the in-situ spectra also show a shoulder in the 402-404 eV range, which is typically attributed to oxidized nitrogen (N-O). However, this peak does not increase upon air exposure, which shows that a different assignment is required for this peak. Instead, air exposure results in the gap between the two main peaks being filled, presumably due to an increase in pyrrole-like nitrogen (>N-H) and/or amino-like nitrogen (>NH$_2$). Meanwhile, the C1s peak broadens on the high-energy side which indicates that the 5-10 at.% oxygen uptake on the film surface is primarily in the form of C-O and possibly H$_2$O, but not N-O.

Argon ion etching readily removes surface oxygen, but also results in a strong preferential sputtering of nitrogen. The N/C ratios rapidly approach equilibria of 0.05-0.2, depending on the initial concentration and the Ar$^+$ beam energy. Furthermore, changes in the N1s peak shape indicate that ion etching causes amorphization of the film surface. Both effects are more pronounced at higher ion energies, and the damage does not appear to be reversible with subsequent low-energy etching. The best methods for evaluating the as-deposited film structure and composition with *ex-situ* XPS will be discussed.

Spectroscopic Ellipsometry Focus Topic
Room: Hall 3 - Session EL-ThP

Spectroscopic Ellipsometry Poster Session

EL-ThP2 Phonon Dispersion and Electronic Band Structure of NiO, ***Stefan Zollner**, A. Ghosh, T. Willett-Gies,* New Mexico State University*, C. Nelson,* University of New Mexico*, L. Abdallah*, New Mexico State University

The phonon dispersion and the electronic band structure of bulk NiO were investigated at 300 K using spectroscopic ellipsometry from the mid-infrared (0.03 Ev) to the near-ultraviolet (6.5 Ev). Since NiO crystallizes in the rocksalt structure, we find a single transverse-optical (TO) phonon at 49 meV with a broadening of 2 meV. There is no evidence of mode-splitting (due to antiferromagnetic ordering, within the broadening of this phonon of 2 meV) or zone folding (due to the doubling of the unit cell). Instead, we find a modification of the reststrahlen band due to TA+TO two-phonon absorption occurring between the TO and LO phonon energies, similar to LiF. Using transmission and ellipsometry measurements, we clearly establish that the lowest direct band gap of NiO occurs at 0.85 Ev at room temperature. The valence band maximum (VBM) of NiO is made up of O (2p) states and the lower Hubbard band of the Ni (3d) states. Direct interband transitions at 0.85 Ev are possible from the valence band to the dispersive Ni (4s) conduction band at the Γ point. A strong peak in the absorption at 3.95 Ev is attributed to transitions from the valence band to the upper Hubbard band (the charge transfer gap of NiO). A derivative analysis of the ellipsometry spectra also shows weak peaks at intermediate energies (between 1.7 and 3.6 Ev), which are attributed to transitions from localized valence band states to the dispersive Ni (4s) band. The charge-transfer gap of NiO shows a temperature dependence very similar to the E$_1$ gap of Si. The absorption between 1 and 3 Ev has a very different behavior, however. The character of the pseudo-dielectric function of NiO changes completely between 700 and 800 K in UHV, where NiO is known to deteriorate due to sublimation. Cooling the sample does not restore the original shape of the dielectric function, but it can be recovered partially by annealing in oxygen.

EL-ThP3 Tribrid EC-QCMD-GSE Analysis: Surface Topography Effects on the Electrochromic Behavior of Methylene Blue, ***Derek Sekora**, A.J. Zaitouna, R.Y. Lai, T. Hofmann, M. Schubert, E. Schubert*, University of Nebraska - Lincoln

The optical and electrical properties of flat and highly ordered, 3-dimensional nanostructured thin films change dramatically upon adsorption of self assembled monolayers (SAMs) to the surface. Here, a tribrid technique consisting of electrochemistry (EC), quartz crystal microbalance with dissipation (QCM-D), and generalized spectroscopic ellipsometry (GSE) is introduced which allows for fundamental analysis of simultaneous electrochemical, optical, and mechanical properties. The electrochromic reduction of methylene blue terminated SAMs on flat and slanted columnar thin film Au substrates is investigated as an example.

The electrochemical redox reaction of methylene blue produces a switch between a blue and colorless SAM, which can be ellipsometrically modeled. Furthermore, a combinatorial tribrid analysis of in-situ step-decreased constant potential scans elucidate the effects of varying the quantity of reduced methylene blue molecules on flat and nanostructured surfaces. The EC and GSE results imply that methylene blue molecules attached deep between Au slanted columns are not as readily reduced as a result of capacitive shielding effects at lower cell potentials. The concurrent in-situ QCM-D response indicates no quantifiable mass transfer as expressed by the Sauerbrey analysis. The results demonstrate that the fluidic tribrid technique allows characterization of conformal coatings on highly ordered nanostructured surface topographies during electrochemical surface modifications. Our approach is perfectly suited for applications including DNA sensing procedures, electrochemical surface reactions, and surfactant effects.

Plasma Science and Technology
Room: Hall 3 - Session PS-ThP

Plasma Science and Technology Poster Session

PS-ThP1 Effect of Embedded Radio Frequency Pulsing for Selective Etching of SiO_2 Contact Hole using $Ar/C_4F_8/O_2$ Gas Mixture in the 60/2 MHz Dual-frequency Capacitively Coupled Plasma System, ***Namhun Kim***, Samsung Electronics, Republic of Korea, *G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

The characteristics of embedded pulse plasma using 60 MHz radio frequency as the source power and 2 MHz radio frequency as the bias power were investigated for the etching of SiO_2 masked with an amorphous carbon layer (ACL) using an $Ar/C_4F_8/O_2$ gas mixture. Especially, the effects of the different pulse duty ratio of the embedded dual-frequency pulsing between source power and bias power on the characteristics on the plasma and SiO_2 etching were investigated. The experiment was conducted by varying the source duty percentage from 90 to 30% while bias duty percentage was fixed at 50%. Among the different duty ratios, the source duty percentage of 60% with the bias duty percentage of 50% exhibited the best results in terms of etch profile and etch selectivity. The change of the etch characteristics by varying the duty ratios between the source power and bias power was believed to be related to the different characteristics of gas dissociation, fluorocarbon passivation, and ion bombardment observed during the different source/bias pulse on/off combinations. In addition, the instantaneous high electron temperature peak observed during each initiation of the source pulse-on period appeared to affect the etch characteristics by significant gas dissociation. The optimum point for the SiO_2 etching with the source/bias pulsed dual-frequency capacitively coupled plasma system was obtained by avoiding this instant high electron temperature peak while both the source power and bias power were pulsed almost together, therefore, by an embedded RF pulsing.

PS-ThP2 Synthesis of B_4C And In Situ B_4C / ZrB_2 From Sugar Based Precursor, ***Abdullah Selim Parlakyigit***, *E. Aktan*, *C. Ergun*, Istanbul Technical University, Turkey

Boron carbide (B_4C) is one of the hardest materials and therefore commonly used for a variety of applications including armor plating, blasting nozzles and mechanical seal faces, as well as for grinding and cutting tools. Conventional production methods of B_4C, such as carbothermal reduction in industrial scale requires high investment and high operating costs, inhomogeneous resultant material, etc.

Zirconium diboride (ZrB_2) is a highly covalent refractory ceramic material which is considered as an ultra-high temperature ceramic (UHTC) with a melting point of 3246 °C. ZrB_2 with its relatively low density of ~6.09 g/cm^3 and good high temperature strength has a potential to be used for high temperature aerospace applications.

In the present study, a method based on sulfuric acid dehydration of sugar was developed to synthesis a precursor material, which can yield B_4C and in situ B_4C/ ZrB_2 composites at much lower temperatures compared to traditional carbothermal methods. The precursor material was heat treated at the temperatures between 1000 and 1600°C under inert atmosphere and characterized by XRD, SEM and FTIR.

PS-ThP3 High Power Pulsed Magnetron Sputtering: A Way to Broaden Industrial Implementation, ***Jake McLain***, *P. Raman*, *I.A. Shchelkanov*, Center for Plasma Material Interactions, University of Illinois, USA, *S. Armstrong*, Kurt J. Lesker Company, *D.N. Ruzic*, Center for Plasma Material Interactions, University of Illinois, USA

High Power Pulsed Magnetron Sputtering (HPPMS) is a magnetron sputtering technique that utilizes high peak power pulses applied to the sputtering target. HPPMS is capable of producing a much higher fraction of sputtered material ions, though has the major drawback of intrinsically low deposition rates for all materials. The low deposition rate is a byproduct of the “return effect”, seen in systems that have high amounts of sputtered ions. [1]. HPPMS provides better film quality, and in some cases enables unique deposition processes. [2] Despite the characteristic better film quality, the inherently low deposition rates obstruct wide industrial implementation.

Center for Plasma Material Interactions (CPMI) has developed the “ε” magnet pack, which is capable of HPPMS deposition rates comparable to DC Magnetron Sputtering (dcMS) deposition rates at 500W and 10mTorr. [3] To achieve that high deposition rate, the “ε” magnetic configuration implements a field topology referred to as “opened field lines”.

All previous research was done in cylindrically symmetric configurations, but most large- scale industrial tools utilize liner magnetrons of up to several meters long. This work is dedicated to the development of a rectangular magnet pack compatible with commercially available magnetrons, in order to provide higher deposition rates of HPPMS in a wider range of technological processes. Electron confinement is discussed in detail, and the sputtering rate from the rectangular pack at different cathode-substrate distances in a HPPMS discharge is modeled.

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PS-ThP4 Non-thermal Plasma Synthesis of Hollow Silicon Carbide Nanoparticles, ***Devin Coleman***, *T. Lopez*, *O. Yasar-Inceolgu*, *L. Mangolini*, University of California - Riverside

The synthesis of beta-phase silicon carbide nanoparticles exhibiting a hollow core-shell morphology is demonstrated by means of a two-step non-thermal plasma method.[1] Crystalline silicon nanoparticles are nucleated from silane precursor gas in a non-thermal plasma reactor similar to the one described in [2] and injected into a secondary methane-containing plasma reactor, where they are carbonized to form beta-phase silicon carbide nanoshells. An analytical solution of the 1D diffusion equation in spherical coordinates, as well as the lattice volume expansion from silicon to silicon carbide are used to explain the formation of the interior void. This provides an alternative to previously reported results, which invoke the nanoscale Kirkendall effect to explain the void formation by means of fast out-diffusion of the core element.[3] Further consideration of the system kinetics indicates interactions with the ionized gas leads to particle superheating, allowing for the diffusion of carbon into the silicon matrix and nucleation of beta-phase silicon carbide to occur during the short residence time of the particles in the system. This work expands upon the materials achievable by non-thermal plasma synthesis and reinforces its potential as an industrial materials processing method. Furthermore, it suggests that such systems offer the capability to engineer particle morphology.

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PS-ThP5 Finite Element Modeling of Surface Wave Plasmas Excited by Microwave Slot Antennas for Processing of Thin Film Materials, ***Pawel Piotrowicz***, University of Illinois, *D. Alman*, *B. Jurczyk*, Starfire Industries, *M. Stowell*, Applied Materials, *I. Schelkanov*, University of Illinois, *D. Curreli*, University of Illinois at Urbana Champaign, *D.N. Ruzic*, University of Illinois

Plasmas generated by microwave excitation offer multiple advantages to thin film processing over lower frequency and DC discharges. Typical microwave discharges create plasmas with higher densities of electrons, lower average electron temperatures, and lower sheath voltages. The decreased ion energies and higher densities respectively offer less ion-induced damage to the thin film and higher deposition rates. These advantages can provide a processing technique to grow high quality crystalline thin films with low density of intrinsic defects.

However, on smaller scale devices, microwave discharges have not been used in industry, due to the difficulty in creating a uniform plasma density. The finite element model describes surface wave plasmas generated by a microwave slot antenna. The plasma is modeled as a dielectric medium with variable plasma density. Dielectric properties of the plasma are derived from a cold plasma dispersion relation. This approach provides a simple model to predict plasma density based on power deposition throughout the dielectric material, which can be used to optimize antenna design for uniform plasma generation.

PS-ThP6 Instantaneous Generation of Many Flaked Particles in Mass-Production Plasma Etching Equipment, ***Yuji Kasashima***, National Institute of Advanced Industrial Science and Technology (AIST), Japan

The mechanism of instantaneous generation of many flaked particles is investigated in mass-production plasma etching equipment. The results indicate that the deposited films are severely damaged and flaked off as many particles when an inner wall potential (floating potential) changes instantaneously and the electric field stress works as an impulsive force.

Particle contamination in plasma etching equipment significantly lowers production yield and overall equipment efficiency. In plasma etching, etching reaction products adhere to the inner chamber walls, gradually forming films as wafers are processed. Particles are generated by flaking of the deposited films due to electric field stress. In mass-production line, serious contamination caused by many particles sometimes suddenly occurs.

The experimental apparatus is the mass-production reactive ion etching equipment which can generate capacitively coupled plasma discharge. The etching process sequence and equipment parameters are similar to those used in actual manufacturing facilities. This study uses a titanium etching process that often causes significant particle contamination in mass-production equipment.

Flaked particles are detected by the in situ particle monitoring system. A sheet-shaped laser beam is introduced in a plane parallel to the wafer in the processing chamber at a distance of 4 mm from the ground electrode. The light scattered by particles is measured using an image-intensified charge-coupled device camera. The viewing port style plasma probe (VP-Probe) can detect a transient change in the floating potential formed on the inner surface of the chamber.

In this experiment, electrostatic chuck voltage much higher than usual is supplied to induce micro-arc discharge at the back of wafer. Many particles are detected simultaneously with the abrupt increase in the amplitude of VP-Probe caused by the micro-arc discharge. The arcing at backside of the wafer and many particles from the ground electrode occur simultaneously. That is, these phenomena occur at the same time despite in different parts of the chamber. The large and rapid change in the inner wall potential due to the arcing can make the electric field stress acting on the deposited film work as an impulsive force, generating numerous flaked particles suddenly.

Accordingly, the results reveal that the floating potential on the inner chamber wall changing rapidly and markedly causes many flaked particles because the deposited films are strongly damaged by the impulsive force of electric field stress. This mechanism can occur on not only a ground electrode but also a chamber walls, and lead to serious contamination.

PS-ThP7 Plasma Chemical Transport of Borazine for 2D Atomic Layer Growth of Hexagonal Boron Nitride, ***Takeshi Kitajima***, *T. Nakano*, National Defense Academy of Japan

Hexagonal Boron Nitride (h-BN) is interested because of its similar 2 dimensional crystal feature to Graphene.

The stack of h-BN with Graphene has less lattice mismatch compared to the other dielectric materials.

Mechanical exfoliation and stacking of h-BN with Graphene is examined and presented a novel transistor characteristics[1]. Chemical vapor deposition schemes are desired for the future mass production of the devices.

CVD growth of h-BN film on Cu or Ni is shown by several groups using Borazine as the source of BN under high temperature atomospheric conditions[2].

In this study, we introduced a new plasma induced chemical transport technique[3] of Borazine to the growth of h-BN for expanding the process window.

The experimental apparatus of the plasma chemical transport consists of the growth chamber and the plasma chamber (Fig.1). The growth chamber has a manipulator with a Mo sample heater. The plasma chamber has inner type 9 turn coil for inductive coupling of 100 MHz RF power. On the side of the coil, Borazine powder is placed to be vaporized by the hydrogen plasma exposure. The pressure of the plasma is 30 Pa. The Borazine vapor and the hydrogen radicals are transported to the growth chamber through 2 mm orifice which suppresses the ion exposure to the sample surface. The growth temperature ranges 560C to 1000C.

The optical microscope image of the film (Fig.2) shows the BN related clusters are locally produced on 560C sample while 1000C sample shows many graphene patches generated from excess carbons from the plasma source. The atomic concentration of the sample (Fig.3) shows the B and N concentration is highest (16 and 12 %) at 560C, and decreases to 3 and 2 % at 730C. Therefore, BN precursors can deposit on Cu surface only at lower sample temperature. This is also confirmed by the Atomic Force Microscope image of the sample (Fig.4). The image shows the 560C sample is covered with BN related polymer islands about a few tens of nm in width. The islands disappear as the growth temperature increases and the terrace of the Cu is emphasized.

The results show that BN growth on Cu with low pressure plasma induced chemical transport of Borazine is only possible at relatively low sample temperature. The 2 dimensional BN film growth is required to start from the BN polymer growth at lower temperature. We expect the BN polymer should be annealed at higher temperature around 1000C and be converted to 2 dimensional atomic layer.

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PS-ThP9 A Low Cost Microplasma Generation Device for Detection of Volatile Organic Compounds Using Plasma Emission Spectroscopy, ***Po-Wei Ye***, *C.C. Hsu*, National Taiwan University, Taiwan, Republic of China

A low-cost and portable dielectric-barrier-discharge-type microplasma generation device (MGD) and the use of this MGD to detector volatile organic compounds are presented. This MGD was made of double-side copper laminate (CCL) and the MGD electrode patterns were defined using the toner-transfer method. Which enables defining the patterns with resolution down to approximately 150 mm without the need of using cleanroom facilitates. Using this MGD with a specially designed electrode arrangement, an applied voltage of 20 kHz and 500 Vrms is sufficient to ignite and sustain stable plasmas in an Argon-rich atmosphere. When the plasma is ignited in Argon atmosphere with a controlled amount of organic compounds addition, carbon-related optical emissions, namely CH(430.29nm) and C2(513.5nm), are observed using a spectrometer. With this MGD, the detection limit for methanol, ethanol, and acetone are 248 48, and208ppm, respectively. A nearly linear calibration curve can be obtained for ethanol with a concentration range from 50 to 1000 ppm.

PS-ThP10 The Development of a Pin-to-Droplet Plasma Generation Device for Detection of Metallic Ions in Aqueous Solutions, ***Min-Chun Chen***, *C.C. Hsu*, National Taiwan University, Taiwan, Republic of China

This work presents a simple set-up and potentially portable plasma generation device for the detection of metallic ions by optical emission spectrometry. This device consists of a needle-type power electrode and a droplet on a metal plate as the ground electrode. With a precisely control of the pin-to-droplet distance of 0.1 to 0.3 mm, the plasma can be ignited with a 2 kV DC voltage in ambient air without the need of any purging gases. . With this device, detection of metallic ions in aqueous solutions can be performed by analyzing the plasma emission spectroscopy with a sample amount as small as 5 µL. Na, Li and K ions with a concentration as low as 20, 70, and 400 µg/L, respectively, can be detected. This detection limit can be significantly decreased when the metallic ions are dissolved in acid such as HNO_3 or HCl. The sensitivity for optical emission spectrometry of different metallic ion is Na>Li>K>Cu>Zn. A linear calibration curve with a concentration between 2 and 2000 mg/L for Na ion by correlating the normalized metallic emission intensities and the concentration has been established. Finally, the potential using this device as a battery-powered and portable analytical tool will be discussed.

PS-ThP12 Simulation of Deep Silicon Etching under Cryogenic ICP $SF_6/O_2/Ar$ Plasma Mixture using multi-Scale Approach, *Y. Haidar*, ***Ahmed Rhallabi***, *A. Pateau*, *A. Mokrani*, Université de Nantes, France, *F. Taher*, Université Libanaise, Lebanon

SF_6 based plasma is widely used in the dry etching of silicon. In many new devices manufacturing such as Systems in Packages (SIP) or Micro-Electro-Mechanical Systems (MEEMS), deep etching of silicon without any local morphological defects like bowing, undercut or trenching is required. Cryogenic silicon etching is used by adding oxygen in order to inhibit the sidewall etching and then improve the silicon etch anisotropy. The fraction of oxygen in $SF_6/O_2/Ar$ plasma mixture is one of the critical parameters in the control of this process.

In order to know more about the plasma surface interaction in cryogenic ICP silicon etching process, we have developed silicon etching simulator. The model is composed of three modules: plasma kinetic model, sheath model and etching model. The plasma kinetic model is based on the 0D global approach which allows the calculation of the average densities and fluxes of neutral and ion species as well as the electron density and temperature in ICP $SF_6/O_2/Ar$ plasma mixture versus the ICP machine parameters. Such output parameters are introduced as input parameters in the sheath model and silicon etching model. Cellular Monte-Carlo method is used to describe the plasma surface interactions in a probabilistic way for silicon etching trough the mask.

The aim of this work is to validate the set of simulation and show the influence of some input parameters (Rf power, pressure, gas flow rates and bias voltage) on the etching processes.

Particular attention is paid on the study of the effect of the oxygen fraction on the evolution of both the $SF_6/O_2/Ar$ plasma kinetic and the silicon etch profile trough the mask. The simulations results show that up to 10% of O_2, diminution of the undercut characterized by the surface etching under the mask is observed while beyond this value, the etching rate is considerably decreased. This is due to the domination of the passivation process by oxygen on the silicon trench bottom.

PS-ThP13 Two Dimentional Visualization of Oxidation Effect of Scalable DBD Plasma Irradiation using KI-starch Solution, *K. Koga, T. Amano,* ***Thapanut Sarinont***, Kyushu University, Japan, *T. Kawasaki,* Nippon Bunri University, Japan, *G. Uchida,* Osaka University, Japan, *H. Seo, N. Itagaki, M. Shiratani, Y. Nakatsu, A. Tanaka*, Kyushu University, Japan

Biomedical applications of plasmas have been extensively explored by applying various plasma sources such as corona discharges, dielectric barrier discharges (DBD), gliding arc, and spark discharges. Quantitative evaluation of oxidation effect of these plasma sources is crucial to select one of the sources appropriate to an application, because most applications employ the oxidation effect. Here we have assessed the oxidation effect of our scalable DBD plasmas using KI-starch solution, the color of which changes from transparent to purple by the oxidation of I^- to I_2 [1]. Experiments were conducted using the scalable DBD device of 40x44 mm^2 in discharge area [2, 3]. 360 μl of solution of 0.5 % potassium iodide and 0.5 % starch was put in each well of a 96 well plate. The well plate was set at 3-10 mm below the electrode and then the solution was irradiated by the discharge plasma. The discharge voltage and current were 9.2 kV and 0.2 A. The discharge duration was 15 s. After the plasma irradiation absorbance at 560 nm of the solution in each well was measured with a plate reader (BioTeK Synergy HT). Two dimensional spatial profiles (71x54 mm^2 in area) of the oxidation effect was obtained by one plasma irradiation experiment. At y= 3 mm below the electrodes the absorbance is nearly constant of 2.6 O.D. under the electrode area, while it sharply decreases to 0.1 O.D. at x= 9 mm outside from the electrode edge x= 0 mm. At y= 10 mm, the absorbance is 2.6 O.D. at the center of the electrodes and gradually decreases even under the electrode area with increasing the distance from the center. It becomes 0.04 O.D. at x= 9 mm. Nonthermal air plasma provides ROS, RNS, charged species and photons to the well plate. Among these species, ROS and charged species are important oxidation species based on the experimental results.

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PS-ThP14 Sensitivity Enhancement of RF Plasma Etch Endpoint Detection With K-means Cluster Analysis, ***Honyoung Lee***, *H. Jang, H. Lee, H. Chae*, Sungkyunkwan University, Republic of Korea

Plasma etch endpoint detection (EPD) of SiO2 and PR layer is demonstrated by plasma impedance monitoring in this work. Plasma etching process is the core process for making fine pattern devices in semiconductor fabrication, and the etching endpoint detection is one of the essential FDC (Fault Detection and Classification) for yield management and mass production. In general, Optical emission spectrocopy (OES) has been used to detect endpoint because OES can be a simple, non-invasive and real-time plasma monitoring tool. In OES, the trend of a few sensitive wavelengths is traced. However, in case of small-open area etch endpoint detection (ex. contact etch), it is at the boundary of the detection limit because of weak signal intensities of reaction reactants and products. Furthemore, the various materials covering the wafer such as photoresist (PR), dielectric materials, and metals make the analysis of OES signals complicated.In this study, full spectra of optical emission signals were collected and the data were analyzed by a data-mining approach, modified K-means cluster analysis. The K-means cluster analysis is modified suitably to analyze a thousand of wavelength variables from OES. This technique can improve the sensitivity of EPD for small area oxide layer etching processes: smaller than 2.0 % oxide area. This technique is expected to be applied to various plasma monitoring applications including fault detections as well as EPD.

PS-ThP15 The Study on the Etching Characteristics of the High Aspect Ratio Amorphous Carbon Layer(ACL), ***Yonghyun Kwon***, *Z.H. Gang, K.S. Shin,* Samsung Electronics Co., LTD., Republic of Korea, *G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

High aspect ratio etch is the key process step in the fabrication of vertically stacked(3D) memory, which is currently the most promising approach for ultra high density and high performance data storage applications. Superior hole dry etch capability, such as wide aspect ratio coverage, good vertical profile control, short throughput, etc, determines the satisfying vertical extendibility, memory cell performance and yield of the 3D memory. The hole etch usually takes a long process time(e.g., >1000 s). Therefore, a fine patterned thick(e.g.,>10um) hard mask must be required. Amorphous carbon layer(ACL) is a proper hard mask material due to its advantageous properties such as high selectivity, ease of deposition and removal and fine profile controllability. In this study, the control knob of thick ACL etch is investigated and solutions for high aspect ratio ACL etch is proposed. By reviewing the scanning electron microscopy(SEM) image after ACL de-capsulation, major/minor axis and the angle is investigated, and ACL tilting and distortion is observed at the aspect ratio 17. A model of ACL tilting induced by wafer warpage and sheath tilting, and ACL distortion formation due to non-uniform indirect ion scattering and by-product deposition is proposed. In addition, possible solutions for improving the ACL tilting and distortion by tuning the bias power, pulse and COS gas flow rate is discussed.

PS-ThP16 Carbon Dioxide and Methane Conversion Using Low Cost Microplasma Generation Devices, ***Yu-Hsin Huang***, *C.C. Hsu, C.M. Wang*, National Taiwan University, Taiwan, Republic of China

Microplasmas offer great potential in gas conversion. In this work, we present the use of a low cost microplasma generation device (MGD) for carbon dioxide and methane conversion. This MGD was made of double-side copper laminate (CCL) and the MGD electrode patterns were defined using the toner-transfer method, which does not require the use of cleanroom facilitates. Two types of system arrangements are tested. In the first arrangement, a MGD was placed in a closed controlled volume with the gas flowing into the system. In the second arrangement, the MGD was integrated with flow channels fabricated on Polydimethylsiloxane (PDMS) devices, which allows for effective plasma-treated gas interaction. With the second arrangement, the conversion of CO_2 was tested at the conditions of 10 KHz and 2.7 KVpp applied voltage, which yields the formation of CO as high as 40000 ppm, which is nearly seven times higher than that obtained using the first arrangement. We will also show the use of these systems to perform the conversion of CH_4 into higher hydrocarbons. Finally, we will discuss the potential using this system for industrial manufacturing processes as a novel platform for gas conversion.

PS-ThP17 A MEMS Approach to Making Quantitative Measurements of IIEE Yields in the Presence of Moderate Electric Fields, ***Keith Hernandez***, *A. Press, D. Urrabazo, M.J. Goeckner, L.J. Overzet*, University of Texas at Dallas

Semiconductor MEMs mechanical switches are prone to failure due to electrical breakdown across gaps between contacts. Electrical breakdown is characterized by Paschen's curve which is a function of both ion induced electron emission (IIEE) yield, electrode spacing, pressure and gas type. Paschen's curve also applies to low frequency microdischarges where the IIEE is one important mechanism of electron emission. Despite the widespread impact of the electrical breakdown phenomenon, few direct measurements of IIEE yield from semiconductors exist. In addition, the semiconductor IIEE yield data currently available do not pertain to practical MEMS or DC microdischarge applications, since the measurements were made on atomically clean and electric field free surfaces. The electric field free aspect of the previous measurements is the result of the macroscopic scale of the electron detection system. To address this issue, we have designed and begun the fabrication of a microfabricated electron detection system (mEDS). This system consists of the basic components of a current-based electron detection system: Electron suppressor- to prevent electrons from escaping collection, an electron collector and sample. A guard layer was also introduced in between the electron suppressor and collector to mitigate leakage current. Unlike previously designed electron detection systems, this device is capable of imposing a controllable uniform electric field (up to 10 V/um). Thus, by integrating the mEDS with an ion source we will have the ability to make IIEE yield measurements under varying electric field conditions. Thus, measurements of field enhanced IIEE and/or ion enhanced field emission become possible. In addition, this mEDS structure can be built on to any substrate that can withstand 250 ^{0}C and high vacuum. This poster will present the design, modeling and fabrication involved in bringing the mEDS to fruition.

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PS-ThP18 Spectroscopic Investigation of Hydrocarbon Plasmas for Coating Applications, ***Sarah Siepa***, Ruhr-University Bochum, Germany, *S. Grosse, M. Guenther,* Robert Bosch GmbH, Germany, *A. von Keudell*, Ruhr-University Bochum, Germany

Diamond-like carbon (DLC) is widely used in coating applications, e.g. as wear-resistant coating on automotive components. One of the common technologies to deposit such layers is by using hydrocarbon plasmas with feed gases such as methane or acetylene. In order to better understand the coating process and to be able to tailor the plasma to the optimum conditions for the specific components, various diagnostic methods are applied to an industrial-scale plasma reactor. Besides probe measurements and Quadrupole Mass Spectrometry (QMS), Optical Emission Spectroscopy (OES) is used. OES investigations have the advantage of being easily applicable even under industrial conditions, where access to the plasma is often limited and homogeneity requires the use of a non-disturbing diagnostic technique. From the spectroscopic measurements and the corresponding model, the excitation dynamics of the plasma is investigated. The plasma parameters electron density and temperature (mean energy) can be determined as a function of input parameters such as pressure, power and gas flow.

PS-ThP19 From Plasma Reactor to Surface Level: Linking Plasma with Feature Profile Simulations, ***Sebastian Mohr***, *A. Dzarasova,* Quantemol Ltd., UK*, D. Tsamados, V. Deshpande, M. Oulmane,* Synopsys LLC, Switzerland*, J. Tennyson*, University College London, UK

Competitiveness in semiconductors industry is based on the ability to quickly integrate advanced technologies in products and optimise manufacturing processes. Only a coherent preparation of these processes allows companies to design successful products. One of the most important steps in the production of semiconductors is the treatment of surfaces by means of plasma processing. The resulting surface profiles usually depend on process parameters such as power or pressure in a non-linear way and are hard to predict. Simulations of plasmas on reactor scale and feature scale modelling of the surface reactions are an alternative to trial and error, saving costs and providing insights in the physical processes. Such simulations require solid input data. In case of plasma simulations, the process parameters are needed; Feature scale models require the flux distributions of particles to the processed surfaces. These flux distributions must be obtained either experimentally, which is not always possible and reliable. Or they are taken from simulations, which requires the output from the plasma simulation to be compatible with the input for the feature scale model. We aim to simplify these investigations by linking two software packages: Quantemol-VT (Q-VT) by Quantemol Ltd. and Sentaurus Topography 3D by Synopsys. Q-VT is a 2D plasma simulation tool, based on the Hybrid Plasma Equipment Model (HPEM) by Mark Kushner [1], which allows the simulation of plasmas in industrial tools on reactor scale level for a wide range of process parameters. The graphical interface of Q-VT allows for an easy setup of HPEM simulations for diverse chamber designs. As a result, Q-VT produces flux distributions of species relevant for surface reactions as a function of both the energy and the angle. These distributions are used as input for Sentaurus Topography 3D, a three dimensional TCAD feature scale etching and deposition simulator for plasma processes used in semiconductor manufacturing: PMC (particle Monte-Carlo) module which is controlled by a set of user-defined surface reactions simulates different phenomena such as adsorption and re-emission, ion reflection, ion-enhanced chemical and physical sputtering, and re-deposition of reaction products, predicting different effects of interest such as micro loading, bowing, micro trenching etc. Linking these two simulations allows comprehensive studies of surface profiles without any additional steps. The validation of the linked tools is currently under progress by comparing its results with published data on common surface processes. First results will be presented.

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PS-ThP20 Atomic Layer Etching of SiO_2 Using Self-Limited Fluorocarbon Films, ***Sanbir Kaler****, Q. Lou, V.M. Donnelly, J. Economou*, University of Houston

Atomic Layer Etching (ALEt) with monolayer accuracy is a critical requirement for advancing nanoscience and nanotechnology. Current plasma etching techniques do not have the level of control or damage-free nature that is needed for patterning delicate sub-10 nm structures with uniform etching rates and higher selectivities. Here we present beam studies of ALEt of SiO_2. Substrates consisting of thin layers of SiO_2 on Si are placed in an ultrahigh vacuum (UHV) chamber, cleaned with an oxygen plasma beam, and then exposed first to a beam of species effusing from a C_4F_8 plasma, followed by bombardment by an Ar^+ beam. The C_4F_8 plasma beam deposits a fluorocarbon (FC) film and the Ar^+ beam removes the film along with a small amount of SiO_2. The process is then repeated. Multiple times between each step, the sample is moved under vacuum to another UHV chamber equipped with x-ray photoelectron spectroscopy (XPS). Changes in FC film thickness and composition are measured as a function of exposure time to the C_4F_8 plasma beam. Similarly, changes are measured in the FC film and SiO_2 film thickness and composition as a function of Ar^+ beam exposure time. The FC film first deposits rapidly, then nearly saturates at a thickness of 0.8 nm and then continues to grow at a much slower steady rate. Stopping at this saturation FC film thickness and exposing the sample to a ~120 eV Ar^+ beam removes 0.08 nm of SiO_2, concomitant with the loss of CF_3 and CF_2 moities (but not of C and F), and then continues to sputter SiO_2 at a much slower rate. The 7:1 F:C ratio observed after 0.8 nm FC film deposition is much higher than the F:C ratio computed from a peak fit of the C(1s) high resolution spectrum (1.3:1), indicating that most of the F is bound in the SiO_2 film. Further details and mechanisms for the ALEt process will be presented.

PS-ThP21 Amorphous Hydrogenated Boron Carbide: A New Color in the Materials Palette for Multiple Patterning, *M.M. Paquette,* ***Bradley Nordell****, T.D. Nguyen, S. Dhungana, A.N. Caruso,* University of Missouri-Kansas City*, W.A. Lanford,* University at Albany-SUNY*, P. Henry, S.W. King*, Intel Corporation

Advanced metal interconnect patterning schemes require a number of materials with specific characteristics and unique etch properties. Currently, many such materials fall within the Si/O/C/N/H phase diagram, and it is becoming increasingly difficult to achieve adequate etch selectivity. Amorphous hydrogenated boron carbide (a-B_xC:H_y) is a unique material with appealing properties for a variety of interconnect applications including a low dielectric constant and excellent mechanical properties. Importantly, because it breaks away from the Si/O/C/N/H stoichiometry, it offers unique etch chemistries, and may therefore represent an important addition to the multiple patterning tool box. We investigate the wet and dry etch behaviors of a-B_xC:H_y films of varying atomic composition and density in comparison with those of silicon-based oxides, nitrides, and carbides.

PS-ThP22 Properties of a Magnetic Neutral-Loop Discharge Plasma, ***Weiyi Li****, S. Kim, J. Blatz,* University of Wisconsin-Madison*, Y. Nishi,* Stanford University*, J.L. Shohet*, University of Wisconsin-Madison

Since Uchida[1] invented the magnetic neutral loop discharge (NLD) plasma in 1994, this technique has been investigated by various approaches. This work utilizes an NLD plasma reactor using a stainless-steel vacuum chamber, instead of the more commonly used quartz chamber in previous work .

The cylindrical vacuum chamber is placed in the middle of three sets of magnet coils. With DC currents flowing in opposite direction in the middle set compared with the ends sets of coils, a circular path on which the magnetic field is zero, *i.e.* a neutral loop (NL), can be produced in the middle of the chamber. In order to generate plasma, 13.56 MHz RF is inductively coupled into the chamber through a quartz window on one end of the chamber with a spiral antenna. The reactor can be operated in three modes, (1) ICP mode when there are no currents in the magnet coils, (2) NLD mode when there is an oppositely directed DC current in the middle magnet coils and the current in the middle is weaker than the currents on the sides, or (3) Enhanced-ICP (E-ICP) mode when current in the middle coils is stronger than currents on the sides. In NLD mode, the plasma was observed to be brighter near the NL than along the axis of the vacuum chamber. In the E-ICP mode, the plasma was observed as bright ball-shape on the axis. This difference was further confirmed with two measurements: The optical spectrum using an OceanOptics spectrometer and the density and temperature using a Langmuir probe. By adjusting the ratio of the DC currents flowing in the magnet coils, the position of the NL can be changed. Both experiment and simulation show that the glow follows the change of NL, especially at low pressure (<1 mTorr).

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PS-ThP23 Impact of Charge Separation Grid Design on Wafer Level Device Performance in an Advanced Plasma Asher, *H-A. Phan-Vu,* ***Shawming Ma***, Mattson Technology

Tradition plasma asher design depends on the grid, or baffle between source and wafer to separate ionized species from activated neutral so more activated neutral is preferred to reach wafer surface to react with photoresist. However, the more you separate the neutral species, the lower the ash rate in general due to loss mechanism during the separation process. In addition, the grid design also controls the ash rate uniformity and affects many other critical device parameters to the final device wafer performance. Therefore, it is extremely important to choose the correct design to the right process application. This paper discussed the impact of advanced plasma asher grid design on the device performance in process uniformity and device response. It is found that grid materials are critical to reduce the ionized species to reach the wafer surface with the conductive grounded grid to be the best for ionized species separation. In addition, the conductive grounded double grid design can not only have better particle and defect performance but also remove any possible UV impact on device from strong UV generated from high ash rate high power recipes. This has contributed to better yield in the production environment down to 10nm technology node.

PS-ThP24 Fluorophore based Sensor for Oxygen Radicals in Processing Plasmas, *F. Choudhury, G. Sabat, M. Sussman,* University of Wisconsin-Madison*, Y. Nishi,* Stanford University*, **J. Leon Shohet***, University of Wisconsin-Madison

A high concentration of free-radicals is present in many processing plasmas, which affects the processing conditions and the properties of materials exposed to the plasma. Determining the types and concentrations of such free radicals is critical in order to determine their effects on the materials being processed. Current methods for detecting free radicals in a plasma require multiple expensive and bulky instruments, complex setups and often, modifications to the plasma reactor. This work presents a simple technique that detects reactive-oxygen radicals incident on a surface from a plasma. The measurements are made using a fluorophore dye (Alexa 488) that selectively reacts with oxygen radicals. It is commonly used in biological and cellular systems for assay labeling in liquids. Using fluorometric analysis, it was found that the fluorophore reacts with oxygen radicals incident from the plasma which is indicated by degradation of its fluorescence. The results show that the fluorescence degrades for about 60 seconds and reaches a constant fluorescence value after which little degradation is observed for longer exposure times. As plasma power was increased, the quenching of the fluorescence significantly increased as expected, because the radicals have higher energies as microwave power was increased. Although they are commonly used in liquid form, the dye can also be immobilized on a surface using an appropriate volatile solvent. Both immobilized and liquid fluorophores were used and the results indicate that both states function effectively under vacuum conditions. The immobilized dye can be 'painted' on a surface and the radical density incident on the surface can be inferred from fluorometric analysis. The immobilized technique can be very useful for many plasma applications - especially when used under vacuum since it prevents the dye from evaporating.

This work has been supported by the Semiconductor Research Corporation under Contract No. 2012-KJ-2359 and the National Science Foundation under Grant No. CBET-1066231.

PS-ThP26 Capacitively Coupled Indirect Plasma Discharge - 2 Dimensional Fluid Model Simulation Study, ***Pei-Siou Luo****, T.Y. Chang,* National Tsing Hua University*, K.C. Leou*, National Tsing Hua University, Taiwan, Republic of China

Capacitively coupled indirect plasma (CCIP) where a grounded mesh is placed between the two electrodes of a conventional CCP have gain a great deal of interests recently for applications where uniform radicals generated by the plasma are needed for material processing while harmful energetic ions or high energy photons should be minimized. In this study, a rf (13.56 MHz) CCIP Ar/H2 discharge has been investigated by numerical simulation based on fluid model, with 12

species and 28 gas phase reactions. Simulation results show that plasma density, as well as the number densities and fluxes of H, important reactive species for applications, increase with rf power, as expected. Simulation Results show that, as a result of the grounded mesh/grid that separating the two chambers, the flux of both ionic and reactive neutral species drop significantly, by a factor of ~1/1000 - 1/10000, from the top main chamber to the bottom drift chamber. More importantly, the plasma density also decreases significantly and the resulting plasma potential in the bottom chamber is only ~10% of that in the top main chamber. This, in term, implies that the ion energy flux incident on the grounded bottom electrode should be minimal, and thus damage to the wafer surface due to ion bombardment can be significantly reduced. Detailed simulation results will be presented.

*Work supported by the National Science Council of ROC.

PS-ThP27 Plasma Simulations with Adaptive Mesh Refinement and Hybrid Kinetic-Fluid Models, ***Vladimir Kolobov****, R.R. Arslanbekov*, CFD Research Corporation

This paper describes the development of plasma simulation tool using adaptive kinetic-fluid models for modern heterogeneous computing systems. The new tool will have a) ability to dynamically switch between fluid and kinetic approaches, b) robust mesh generation and adaptive mesh refinement algorithms, c) implicit solvers adapted for massively parallel CPU-GPU systems.

For gas dynamics in mixed rarefied-continuum regimes, our Unified Flow Solver (UFS) combines a tree-based algorithm of Adaptive Mesh Refinement (AMR) with cell-by-cell selection of kinetic (Boltzmann) and fluid (Navier-Stokes) solvers [1]. This Adaptive Mesh *and* Algorithm Refinement (AMAR) methodology provides the highest level of adaptation to the solution being computed. The kinetic module in UFS can solve kinetic equations by either the Discrete Velocity Method (DVM) [2] or by the statistical particle methods (such as Direct Simulation Monte Carlo (DSMC)) [3]. We have ported the kinetic solvers to Graphics Processing Units (GPU) and demonstrated double digit speedups on single GPU and good multi-GPU scaling [4].

The extension of AMAR to plasma simulations poses extra challenges due to disparity of electron and ion/neutral masses [5]. In this paper, we will show examples of plasma simulations with AMR capabilities using multi-fluid plasma models and describe the implementation of an implicit electrostatic Particle in Cell with Monte Carlo Collisions (PIC-MCC) module. The capabilities of the new PIC-MCC module will be demonstrated for positive column of DC discharges in weakly-collisional regime. We will describe algorithms for porting the PIC-MCC module to GPU and evaluate acceleration that can be achieved. Finally, we will discuss physics-based criteria for the kinetic-fluid decomposition for hybrid plasma simulations.

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PS-ThP28 Meshed Shielding Grid Added Electron Beam Excited Plasma Apparatus for Neutral Nitriding of Precision Components*,* ***Petros Abraha***, Meijo University, Japan

In this research, a customized equipment that utilizes electron beam gun and processing chamber with a meshed shielding grid that comprises of a discharge region, acceleration region and processing region is used to perform diffusion based nitriding treatment of steel components.

The electron beam gun starts discharge when an argon gas is introduced into the discharge region, and DC voltage is applied between the heated cathode and the discharge electrode. Argon is then ionized resulting in a large number of electrons in the discharge region. The electrons are then accelerated by the acceleration voltage Va applied between the discharge electrode and the anode. The generated electron beams are delivered into the processing chamber to produce nitrogen plasma. The plasma nitriding apparatus includes a meshed electrode mounted on the stage and electrically insulated from the processing chamber. The meshed shielding grid is made of stainless and formed into a cylindrical shape. The metal mesh is formed of a wire which has a diameter of 0.16 mm and having 40 meshes per inch. The sample to be treated is placed in the meshed electrode. The plasma nitriding apparatus includes a DC power supply device that bias the sample to a positive potential higher than the plasma potential at the location where the sample is set within the meshed shielding grid. The plasma nitriding apparatus also includes DC power supply that biases the meshed shielding grid to a negative potential.

The results of the nitrided samples, within the meshed shielding grid, for 3, 6, and 12 hours show that the treated surfaces were without any compound layer but composed of only diffusion layer whereby the measured thicknesses were about 45 µm, 65 µm and 90 µm respectively. For comparison, samples were treated under the same conditions but without the meshed shielding grid. The results reveal that in addition to the diffusion layer of about the same thickness, a 5 µm thick compound layer was formed in all three samples. This confirms that the meshed shielding grid is effective in diffusion based nitriding.

PS-ThP29 Deposition of Silicon Nitride Coatings by Pulser Laser Deposition Technique, ***Johans Restrepo***, Universidad Nacional Autonoma de Mexico*, E. Camps,* Instituto Nacional De Investigaciones Nucleares, Mexico*, S. Muhl*, Universidad Nacional Autonoma de Mexico

The Silicon Nitride present problems to be deposited by Pulsed Laser Deposition (PLD) Technique using a pure nitrogen atmosphere and silicon target because the low nitrogen reactivity produce a partial oxidation during the deposition such as the oxygen amount reach values around to 20at%. The aim of this research was deposited silicon nitride at different nitrogen pressure and energy density to found the deposition parameters to reduce the oxygen included on the coatings. The coating were characterized by perfilometry, Routherford Back Scattering (RBS), Raman Spectroscopy, UV-bis Spectroscopy and Nanoindentation while the Plasma properties were characterized by Langmuir probe and Optical Emission Spectroscopy (OES). The OES results showed that the maximum nitrogen activity is reached at $4x10^{-3}$mbar (N_2^+ 391.4nm) and decrease at the nitrogen pressure increase. The average ion kinetic energy and the plasma density decrease from 120 to 100eV and $3.26x10^{13}$ to $4.89x10^{11}$ ion/cm^3 at nitrogen pressure of $4x10^{-3}$ and $6x10^{-2}$ mbar respectively.

Surface Modification of Materials by Plasmas for Medical Purposes Focus Topic

Room: Hall 3 - Session SM-ThP

Surface Modification of Materials by Plasmas for Medical Purposes Poster Session

SM-ThP1 Replacing Self-Assembled Monolayers by Functional Plasma Polymers in Fabrication of Immunosensors, ***Lenka Zajickova***, *A. Manakhov, E. Makhneva, D. Kovar,* Masaryk University, Czech Republic, *G. Dorozinsky, O. Shynkarenko, G. Beketov,* Lashkaryov Institute of Semiconductor Physics, Ukraine, *P. Skladal*, Masaryk University, Czech Republic

Plasma polymerization is an efficient way to the modifications of various surfaces by desired functional groups. It finds potential applications in tissue engineering or fabrication of biosensors. This work reports on the plasma polymerization of two functional coatings that were used as a replacement of self-assembled monolayers (SAMs) in the fabrication of immunosensors. Amine-based coatings were deposited from cyclopropylamine mixed with argon in low pressure capacitively coupled discharge whereas carboxyl-based coatings were prepared by co-polymerization of maleic anhydride and acetylene in atmospheric pressure dielectric barrier discharge. The coatings were prepared on gold surfaces of either quartz crystal microbalance or surface plasmon resonance sensors. Their performance was tested on a model system, monoclonal antibody (Ab AL-01) against human serum albumin (HSA) interacting with the corresponding HSA antigen. The immobilization of antibodies and inactivation of free non-reacted groups was realized in buffers with various pH. A crucial point was the stability of the prepared plasma polymers in liquids that was studied by time-varying sensor response and also by physical characterization methods (X-ray photoelectron spectroscopy, infrared spectroscopy, atomic force microscopy, ellipsometry) in the dry state. The performance of the immunosensors with the plasma polymer layers were compared to the sensors prepared using the standard procedure using SAM.

Scanning Probe Microscopy Focus Topic

Room: Hall 3 - Session SP-ThP

Scanning Probe Microscopy Poster Session

SP-ThP1 Extreme Magnetic Properties of Co Atoms on MgO Films, ***Christopher Lutz***, *S. Baumann, A. Heinrich, W. Paul, T. Choi*, IBM Research - Almaden

The magnetic moment of a free atom arises from the spin and orbital angular momentum. In a solid state environment, anisotropy in the orbital moment due to the ligand field, together with spin-orbit coupling, gives directionality and stability to the magnetization. Here we use a low-temperature scanning tunneling microscope (STM) to show that Co atoms bound to O sites on a MgO layer achieve a record-high zero-field splitting of 58 meV, which closely approaches the theoretical limit given by the spin-orbit coupling in a 3d transition metal atom. The zero-field splitting gives the energy of the first quantum step required to surmount the anisotropy barrier and reverse the magnetization. The combination of large moment and large anisotropy energy results in magnetic-state lifetimes exceeding 0.2 ms. The high symmetry of the Co atom's binding site gives a ligand field that is effectively cylindrical, which yields a large axial anisotropy while preserving nearly all of the free-atom's orbital angular momentum. All-electrical pump-probe measurements reveal the large magentic moment (5.5 µB) directly in STM. These results provide a symmetry-based strategy for the design of stable nanomagnets.

SP-ThP2 High Resolution qPlus NC-AFM with a New Cryogen-Free Variable Temperature UHV SPM, *C. Troeppner, M. Atabak, S. Molitor, J. Koeble,* ***Bjoern Piglosiewicz****, J. Chrost*, Oxford Instruments

We present first qPlus[1] NC-AFM results of a new cryogen-free cooled ultra-high vacuum compatible scanning probe microscope capable of high stability STM and qPlus NC-AFM operation at temperatures ranging from low temperature up to above room temperature.

The microscope features a cold-sample and cold-tip design. Overcoming the limits of hold time of cryogenic liquids by the cryogen-free approach this microscope provides access to new classes of experiments. Combining drift values much smaller than 1A/h and stable tip conditions enable e.g. unsurpassed long-term spectroscopic SPM measurements.

Decoupling the strong mechanical vibrations induced by the pump of the closed cycle cooler represents a major technical challenge. Our design of the cryogen-free microscope effectively decouples the inherent mechanical vibrations to a level of state-of-the art low temperature SPM's utilizing cryogenic liquids.

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SP-ThP3 Surface Reconstruction for Accuracy Improvement in Nanoparticle Size Characterization, ***James Su***, *N.N. Chu, C.T. Lin, P.L. Chen, M.H. Shiao, C.N. Hsiao, F.Z. Chen*, Instrument Technology Research Center, National Applied Research Laboratories, Taiwan, Republic of China

In this study compares the analytical results of atomic force microscopy (AFM) and scanning electron microscopy (SEM) for characterizing size distributions of various nanoparticles in the size range of (10 – 300) nm. Polymer nanospheres, mixture of colloidal gold and GaN quantum dots were characterized by both techniques. Both techniques were recalibrated with transfer standards traceable to the international metrology institute PTB where the combined uncertainty of measurement results were less than 1%. Average SEM values for mono-size dispersed particles of polymer and gold were slightly lower than the nominal values where AFM values were slightly higher on the contrary. Additional AFM deconvolution process has efficiently reduced the slight broadening of measurement results due to tip effects. Supported by comparisons to published data obtained on quantum dots of increasing diameters, the results show that the apparent size of small details appears to be larger than their actual dimension and the apparent distance between small objects may appear less than their actual dimension. The same method allows us to develop strategies to minimize the errors when the dimension of details is of less the order than the effective resolution of the operated SEM. Most of the size distributions were easily identified with AFM, and the modified average particle size for mono-size dispersed particles is in a good agreement with the nominal values. AFM characterization of nanoparticles using effective deconvolution process and statistical analysis software provides both accurate and rapid analysis for nanoparticle characterization.

Thin Film

Room: Hall 3 - Session TF-ThP

Thin Films Poster Session

TF-ThP2 The Nano-power Generator Fabricated with Thin Atomic Layer Deposited Films, ***Giovanna Scarel***, James Madison University

The energy of low power infrared (IR) radiation can be transferred to a power generator (PG) device and transformed into usable power [1, 2]. This process, called IR power generation, is demonstrated with commercially available PG devices [1, 2]. However, active media, such as Nb-doped TiO_2 films, can be fabricated in the form of thin films [3]. Voltage production through IR power generation was recently realized using atomic layer deposited (ALD) films [4], but not optimized. This poster outlines the strategies in terms of film architecture and fabrication method that can be employed to increase the efficiency of nano-PG devices fabricated via ALD.

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TF-ThP3 Influence of Deposition Time on the Microstructure of Electrodeposited ZnO Films and p-Si/n-ZnO Heterojunction Diode Fabrication, ***Saliha Ilican***, *Y. Caglar, S.A. Aksoy, M. Caglar*, Anadolu University, Turkey

ZnO is one of the widely studied materials for its number of exciting properties. It is a wide band gap semiconductor material with $E_g \sim 3.3$ Ev. Electrodeposition is well known for depositing metals and metallic alloys at the industrial level, with a wide range of applications from large area surface treatments to most advanced electronic industries. Electrodeposition of semiconducting materials thus represents a new challenge, not only from the academic point of view, but also from the economic point of view, since this method presents interesting characteristics for large area, low cost and generally low temperature and soft processing of materials. ZnO nanorod array films were grown by electrochemical deposition onto p-Si substrates from an aqueous route. Aqueous solution of $Zn(NO_3)_2.6H_2O$ and hexamethylenetetramine (HMT) was prepared using triple distilled water. The bath temperature is maintained at 90 ºC during the electrodeposition of the ZnO films. The effect of deposition time on the crystallinity and nanorod arrays were investigated. The crystalline structure and orientation of the ZnO films were investigated using XRD method. The lattice parameters and texture coefficient values of the films were determined. Microstructure was analyzed by a field emission scanning electron microscope (FESEM), and the effects of the deposition time in the microstructure of the films were investigated. The film was determined the most appropriate structural properties and the p-n heterojunction diode was fabricated by using this film. The diode parameters were determined from the analysis of the measured dark I-V curves. Rectifying behavior was observed from *I-V* characteristics of these heterojunction diodes.

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TF-ThP7 The Effect of Nickel Content on Structural and Optical Properties of ZnO Films by Sol Gel Process, ***Seval Aksoy***, *Y. Caglar, M. Caglar, S. Ilican*, Anadolu University, Turkey

Semiconductor materials have received much attention because of their novel properties. Zinc oxide (ZnO) has been attracting attention because of the commercial demand. It is well known that the addition of impurities into a wide band gap semiconductor. A selective doping element into ZnO has become an important route for enhancing and controlling its structural, morphological, electrical, and magnetic performance. The magnetic property in III–V semiconductors do not attract much attention for device fabrication. Ni is an important dopant in the magnetic materials. Additionally, Ni2+ (0.69 Å) has the same valence compared to Zn2+ and its radius is close to Zn2+ (0.74 Å), so it is possible for Ni2+ to replace Zn2+ in ZnO lattice.

In this work, undoped ZnO and Ni doped ZnO (ZnO:Ni) films have been deposited by sol–gel method using spin coating technique. As a starting material, zinc acetate dihydrate was used. 2-methoxyethanol and monoethanolamine were used as a solvent and stabilizer, respectively. The dopant source of Ni was nicel (II) acetate tetrahydrate. The effects of Ni concentration on the crystal structure and orientation of the ZnO films have been investigated using X-ray diffraction (XRD) study. The crystal structure and orientation of the ZnO film were determined to be a hexagonal wurtzite structure and a preferred orientation of (002). The average crystallite size, texture coefficient, dislocation density and lattice constants of the ZnO:Ni films were calculated. The average crystallite size values for the films was found to be in the range of 33–42 nm. The highest grain size value was obtained for the undoped ZnO film. Surface morphology of the films has been also studied by a field emission scanning electron microscope (SEM). The transmittance spectra of the films were measured to investigate their optical properties. All the films are highly transparent with average transmission (>81%) in the visible range. The optical constants of these films were determined using transmittance and reflectance spectra.

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TF-ThP8 Effect of Applied Voltage on the Structural and Morphological Properties of Electrodeposited ZnO Films, ***Pinar Bilgic Ozden***, *Y. Caglar*, Anadolu University, Turkey

ZnO is a widely used and produced n-type semiconductor material which can be obtained by several deposition techniques. Among them electrochemical deposition technique is one of the most promising technique for depositing ZnO because of the simplicity of the experiments and lower cost. It is possible to obtain high quality films by changing deposition parameters.

In this study, ZnO films were electrodeposited onto 100nm thick tin doped indium oxide (ITO) coated glass substrate via electrochemical deposition technique. Hexamethylenetetramine ($C_6H_{12}N_4$) and zinc nitrate hexahydrate $Zn(NO_3)_2.6H_2O$ salts were used as precursors in a 90°C aqueous solution. In our experimental setup, potassium chloride saturated silver/silver chloride (Ag/AgCl) electrode, a platinum (Pt) wire and ITO substrate were used as reference, counter and working electrodes, respectively. Experiments were carried out at -0.8, -0.9, -1.0, -1.1 and -1.2V for 90min of deposition time. After the depositions process, Structural and morphological properties of the ZnO films were investigated using Bruker D8 Advance XRD and Zeiss Ultra Plus FESEM.

From FESEM images, it is observed that as the applied voltage increase, the amount of the deposited film increase as well, but lower voltage values lead to insufficient coatings. XRD patterns reveal that films which deposited up to -1.0V applied voltage were grown along (002) orientation. Higher applied voltage values caused films to lost some part of their layers, it is probably the main reason of the weak diffraction peaks. As a result -1.0V applied voltage is found to be the best voltage value for this technique with using the parameters and materials mentioned above.

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TF-ThP10 Self-Assembled ZnO Nanoparticles Embedded in a Silicon Oxide Matrix Produced by Reactive RF Sputtering*, *A. Lara-Sanchez,* Facultad de Ingenieria, Universidad Autonoma de Chihuahua, Mexico*, A. Hernandez-Hernandez,* Escuela Superior de Apan, Universidad Autonoma del Estado de Hidalgo, Mexico*, A. Garcia-Sotelo, E. Campos, S. Gallardo-Hernandez,* Departamento de Física-Cinvestav-IPN, Mexico*, M. Zapata-Torres, J.L. Fernandez-Muñoz,* CICATA-IPN, Legaria*, E. Valaguez-Velazquez,* UPIITA-IPN*,* ***MiguelAngel Melendez-Lira***, Departamento de Física-Cinvestav-IPN, Mexico

Self-assembled silicon and germanium nanoparticles embedded within a SiO2 matrix taking advantage of surface roughness have been successfully produced taking advantage of the roughness associated with the sputtering deposition process[1,2]. The aforementioned approach has been employed to explore the possibility to produce ZnO nanopartic les embedded within a silicon oxide matrix on soda-lime glass and p-silicon substrates. Silicon dioxide and metallic Zn films were deposited employing silicon and zinc targets. Oxygen content of the working plasma was modulated through argon partial pressure. X-ray diffraction characterization do not shown the presence of metallic zinc. Secondary ion mass spectroscopy shown an interdifussion of zinc throughout the SiO2 matrix. TEM micrographs indicated the presence of nanoparticles. XPS shown ZnO formation under specific growth parameters. Photoluminescence emission at room temperature for samples grown on silicon substrates was not observed. Transport properties were studied measuring the IvsV characteristics of the films. For samples grown on silicon rectifying behavior and spectral response are observed . The observed results of photoluminescence and transport properties are discussed in terms of the crystalline structure of the ZnO nanoparticles and its interaction with SiO2 matrix.

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TF-ThP11 Development of Dispersed C60/TiAlN Nano-Composite Thin Films with Superior Mechanical Properties, ***Yuki Ishiyama***, *A. Matsumuro*, Aichi Institute of Technology, Japan

We have succeeded in the development of innovative dispersed C_{60} molecule nano-composite Al and TiN thin films with great high hardness and excellent tribological properties. Fabrication method of their composite films has been used by our original unique vacuum evaporation method with both RF magnetron sputtering source and heat evaporator source. Nano-indentation hardness of 1.0 wt.%C_{60}/Al nano-composite thin film showed increased up to 3 times larger than that of Al film. And 2.0 wt.%C60/TiN nano-composite thin film, both nano-indentation hardness and tribological properties increased up to 30 % larger than those of a conventional TiN thin film. These results clearly indicated that dispersion of C_{60} molecules in the conventional films contributed improvement in mechanical properties.

In our study, we challenged to apply the established techniques to fabricate nano-composite materials using C_{60} to TiAlN, which is harder than TiN. Development of the synthesis method of C_{60}/TiAlN nano-composite thin films with the excellent mechanical properties more than those of TiN nano-composite must give effective industrial contributions. C_{60}/TiAlN nano-composite thin films with constant thickness 200 nm were deposited on Si(100) water-cooled substrates using by the same method with both Ti and Al sputtering targets for 30 minutes. The concentrations C_{60} molecule powder were changed in the range from 0.5 to 40 wt.%, and the evaporation temperature was controlled in the range of 523-723 K. The structure analyses of all nano-composite thin films showed that XRD patterns indicated only TiAlN crystalline structure and absorption peaks estimated by FT-IR also corresponded to those of C_{60} molecule. From these results, the microstructures of C_{60}/TiAlN nano-composite thin films were confirmed to consist of both C_{60} molecule and TiAlN crystalline metallic compound. Nano-indentation hardness made clear that the hardness of the composite films of 2.0 wt.%C_{60}/TiAlN showed the maximum hardness of 20 GPa and this value was increased up to 20 % larger than that of TiAlN thin film. Furthermore, tribological properties were also increased up to 20 % larger than that of TiAlN.

On the basis of remarkable results of the previous researches and the present results, it clearly indicates that C_{60} nano-composite is extremely effective in great mechanical properties improvement to dispersed C_{60} uniformly in matrix conventional thin films. Therefore, this study let us know one of bright future view of development of the innovative great hard composite thin films using by C_{60} molecules.

TF-ThP12 Interface of Mo/Si Multilayer formed by Magnetron Sputtering for Extreme Ultraviolet Lithography, ***Chao-Te Lee**, D. Chiang, P.-K. Chiu, H.P. Chen, C.N. Hsiao,* National Applied Research Laboratories, Taiwan, Republic of China, *H.-B. Zhang, C.-C. Jaing*, Minghsin University of Science and Technology, Taiwan, Republic of China

The periodic Mo/Si biilayers with Ru capping layer were deposited on Si (100) substrate by RF magnetron sputtering with Mo, Si, and Ru targets. The multilayers were designed for reflectivity at the wavelength of 13.5 nm. The effects of Ru capping layer on the microstructure, surface roughness and reflectance of multilayers were investigated by atomic force microscopy (AFM), high resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), and a spectrometer. The surface roughness of Ru thin film was decreased from 0.35 nm to 0.15 nm when the RF power was increased from 50 W to 200 W. The AFM measurements showed the uniform morphology with a very low surface roughness value under 0.15 nm with 50V dc-bias assisting. It was found that the Mo-on-Si, Si-on-Mo, and Ru/Si interface layers were discriminated by HRTEM, and XPS. The Mo-on-Si interface layer was 0.45 nm. However, the Si-on-Mo interface layer was increased with thickness increased from 0.9 nm to 1.35 nm. The cause of Mo/Si and Ru/Si interfaces form was attributed to the substrate temperature was increased during sputtering. In this work, the reflectivity of the multilayers was 60 ~ 65 % which was attributed to form the Mo/Si and Si/Ru interfaces.

TF-ThP13 Influence of Cu Doping on the Electrical Transport Properties of Transparent ZnO Nanocrystalline Films Prepared by Sol-Gel Spin Coating Process, ***Chung-Yuan Kung***, Department of Electrical Engineering, National Chung Hsing University, Taichung, Taiwan, Taiwan, Republic of China, *S.L. Young, H.H. Lin*, Department of Electronic Engineering, Hsiuping University of Science and Technology, Taichung, Taiwan, Taiwan, Republic of China

ZnO and $Zn_{0.98}Cu_{0.02}O$ nanocrystalline films were separately deposited on the glass substrates by sol-gel spin-coating technique for the exploration of Cu doping effect. X-ray diffraction patterns of the films show the same wurtzite hexagonal structure and preferential orientation along the *c*-axis. The grain size of ZnO and $Zn_{0.98}Cu_{0.02}O$ films are 52.3 and 126.4 nm calculated by Scherrer Formula, respectively. The increase of grain size induced by Cu doping result can be also observed by SEM images. Hall mobility and carrier concentration of the *p*-tpye $Zn_{0.98}Cu_{0.02}O$ films decrease and resistivity increase as Cu doping due to the increase of defects examined by photoluminescence spectra. Temperature dependence resistivity reveals a semiconductor transport behavior for both nanocrystalline films. Exponent relationship $\sigma(T)=\sigma_{h0}\ \exp[-(T_0/T)^{1/4}]$ at low temperature region and Arrhenius equation $\sigma(T)=\sigma_0\ \exp[-(E_a/Kt)]$ at high temperature region are both fitted well, which separately reveals Mott variable range hopping behavior and thermal activation conduction. Activation energy E_a increases from 46 meV for ZnO to 124 meV for $Zn_{0.98}Cu_{0.02}O$ calculated by Arrhenius equation, respectively. The results demonstrate that the crystallization and the corresponding carrier transport behavior of the $Zn_{0.98}Cu_{0.02}O$ films are affected by Cu doping.

TF-ThP14 Design and Fabrication of MgF_2 Protected Aluminum Mirrors for the DUV Spectral Range, ***Hung-Pin Chen**, W.H. Cho, C.N. Hsiao,* National Applied Research Laboratories, Taiwan, Republic of China, *C.C. Lee*, National Central University, Taiwan

Protected or enhanced aluminum is widely used for the preparation of highly reflective coatings in the DUV spectral range. The obvious choice for a coating with high reflectance above DUV Spectral Range is Al protected with MgF_2. This article presents our preliminary experimental studies on processes to produce MgF_2 protected aluminum mirror, the focus is placed on high reflective coatings for the DUV wavelength range above 125nm to 325nm. Aluminum layers protected with fluoride coatings have been deposited by Ion beam-assisted deposition, all the samples were deposited on fine polished fused silica substrate. The optical parameters of optical interference coatings were optimized using admittance loci analysis by the Essential MacLeod software. The corresponding properties of the films were investigated by in situ optical monitoring, surface quality of the layers has been judged by means scanning electron microscopy, and atomic force microscopy scanning. The reflectance results were measured at the BL04B Beamline of National Synchrotron Radiation Research Center (Taiwan) in DUV spectral region. The highest average reflectance of the DUV reflector (with protect coating) is about 80%. Interference coatings were added to the basic protected Al design to enhance the reflectance.

TF-ThP15 Reliability Analysis of Zinc Tin Oxide Thin Film Transistor under Mechanical Stress and NBIS (Negative Biased Illuminated Stress) Condition, ***Sungmin Kim**, H.J. kim*, Seoul National University, South Korea

Amorphous zinc tin oxide (ZTO) attracts attention as a new channel material of switching thin film transistor (TFT). It has remarkable properties like high field effect mobility (>10 cm^2/Vs) as well as high uniformity and low processing temperature. In this study, electrical properties like threshold voltage (V_{th}), mobility, and subthreshold swing of ZTO TFTs with/without mechanical stress were investigated to find the effects of the photo-bias instability of ZTO TFTs on their mechanical stress.

The fabricated ZTO TFTs have a bottom gate and top contact configuration. Thinned Si wafers of 50㎛ thickness were used as substrates to allow ZTO TFTs to be flexible. To measure the effects of mechanical stress to electrical properties and photo-bias instability, the negative biased illuminated stress (NBIS) tests were performed in three illumination conditions with the photo-wavelengths of 400, 450 and 500 nm as well as in two mechanical bending directions, parallel and perpendicular to a channel width of TFTs, with a bending curvature of 40mm.

Under a mechanical strain, a mobility and a subthreshold swing of ZTO TFTs remained unchanged, but a V_{th} showed noticeable changes. Tensile strain under the bending parallel to a channel width caused more severe photo-instability with more V_{th} shift. V_{th} of ZTO TFTs remained unchanged under the 500nm NBIS condition, while for 400 and 450 nm NBIS conditions V_{th} shifted with a mechanical strain. Particularly, parallel bending of ZTO TFTs under the 400nm NBIS condition showed severe instability, a large and negative V_{th} shift of –11.6V compared to –7.2V of a non-bended sample. And for the 450 nm NBIS condition, relatively small V_{th} shift of –6.1V and -4.4 V for bended and non-bended samples, respectively, was observed, showing similar tendency to the 400nm case. But in case of the bending perpendicular to a channel width showed less V_{th} shift from non-bending condition; -15.8 V to -15.2 V and -5.5 V to -4.0 V for the 400nm and 450 nm NBIS conditions, respectively.

The exact mechanism of this phenomenon is not clear at this point, but the strain in film might change the distance between metal atoms, causing the variation of an orbital overlap in the bandgap and an activation energy for V_{th} shift. G. Zhang et al. reported that a strain in a channel layer makes difference of ZnO band structure like midgap states from the first principle simulation. The tensile strain can cause more midgap levels in bandgap, and vice versa. It is in a good agreement well with our result. The more reasonable mechanisms of strain to affect the band structure is under investigation.

TF-ThP17 Laser Surface Modification of AZ31B-H24 for Improved Corrosion Resistance, ***Michael Melia***, University of Virginia, *N. Birbilis,* Monash University, Australia, *J.R. Scully, J.M. Fitz-Gerald*, University of Virginia

The development of Mg alloys has been accelerated over the last decade due to the need for significant weight reduction of structural components. One long-standing obstacle regarding the use of Mg alloys for widespread field application is their intrinsically poor corrosion resistance and lack of surface films or oxides. Micro-galvanic induced “self-corrosion” due to alloy heterogeneity is a key concern. Therefore, chemical and structural homogenization is of long standing and great interest. Furthermore, there is a need to exploit possible benefits of low fluence LSM, local composition variations and LSM processing gas environments on corrosion behavior. Here we report on the effect of laser surface modification (LSM) on the corrosion resistance of an Mg alloy (AZ31B-H24).

Samples were processed with a pulsed excimer laser operating at 248 nm and a fluence = 1.5 J/cm^2. Microstructure and composition were characterized with scanning electron microscopy (SEM), grazing incidence X-ray diffraction (GIXRD), and energy dispersive spectroscopy (EDS). Corrosion analysis was performed in a standard three electrode corrosion cell in quiescent 0.6 M NaCl solution. Electrochemical Impedance Spectroscopy (EIS) and potentiodynamic polarization measurements were used to determine corrosion resistance, anodic/cathodic behavior, pitting potential and open circuit potential (OCP). Corrosion experiments were imaged by optical video microscopy during testing to draw conclusions regarding the breakdown of the irradiated surface.

Layered structures of nanoscale MgO, Mg_3N_2, andAlN constituents formed in the irradiated region as a function of process gas and proximity to the Al_8Mn_5 intermetallic particles (IMPs). Partial homogenization of IMPs was observed, reducing the initial particle size by 40-60% and creating large areas of Al/Mn enrichment, irrespective of process gas used (Ar, N_2). The results show that a reduction in the H_2 evolution reaction rate was achieved correlated with an order of magnitude decrease in the cathodic current density, as well as a 100 mV to 200 mV reduction in the open circuit potential over short immersion times of up to 4 hours, irrespective of processing gas. In addition, Impedance results support these findings with a 4 and 25 fold *increase* in the polarization resistance after processing in both N_2 and Ar atmospheres respectively. The behavior in full immersion has not been extrapolated to long term field testing.

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TF-ThP18 Enhanced Mechanical Properties of Boron Doped Amorphous Carbon Films by UV Laser Annealing, ***ChulMin Youn**, T. Choi.,* Sejong University, Republic of Korea*, J.Y. Yang,* TES Co. Ltd., Republic of Korea*, K.P. Park, G.H. Hur*, TES Co., Ltd., Republic of Korea

The hard forms of amorphous carbon (a-C, diamond like carbon) include hydrogenated amorphous carbon (a-C:H) and tetrahedral amorphous carbon have raised interest as coating materials. Recently, boron doped amorphous carbon films have been studied as hard mask materials of 3D vertical NAND flash memory. Hard mask was demanded to enhance critical dimension (CD) uniformity, anti-etching and lifting while decreasing thickness. Boron has been widely known efficient dopant for passivating the oxidation of various carbon materials. We have prepared boron doped amorphous carbon film deposited with the fixed B_2H_6 flow rate as a function of the process temperature using plasma enhanced chemical vapor deposition (PECVD). We investigated the physical and optical properties of film with the refractive index, hardness and chemical bonding configuration. Especially, the effect of ultraviolet (UV) laser annealing on the hardness was studied. UV annealing caused a change of chemical bonding configuration, i.e., sp2/sp3 bonding ratio and C-H bonds, through analysis of the Fourier transform-infrared (FT-IR) and RAMAN spectrum. It is found that a significant enhancement of hardness could be attributed to surface confined graphitization and increase of the sizes of sp2 and sp3 clusters, which occur without any damage of surface and delamination of films. In addition, the influence of laser annealing on the stress relief behavior and electronic properties of boron doped amorphous carbon layers will be discussed. Our approach can offer easy control of surface properties of amorphous carbon materials.

TF-ThP19 Influence of Zn(O,S) Buffer Layers on the Performance of $Cu_2ZnSn(S,Se)_4$ Earth-abundant Thin Film Solar Cells, *H. Hong,* ***Jaeyeong Heo***, Chonnam National University, Republic of Korea

A solar cell is an electrical device that converts light energy into electricity. One of the crucial parts of realizing high-performance thin-film-based solar cells is an *n*-type buffer layer. Instead of the widely used, but toxic CdS buffer layer, we investigated the possibility of using Zn(O,S) as an alternative material grown by atomic layer deposition (ALD). First of all, structural, electrical, chemical, and optical properties of Zn(O,S) thin films were studied. In addition, this new buffer layer was applied for earth-abundant $Cu_2ZnSn(S,Se)_4$ solar cells and the highest power-conversion efficiency (PCE) of ~2.7% was achieved by optimizing oxygen-to-sulfur (O/S) ratio. Detailed device analysis which includes current-voltage (J-V), external quantum efficiency (EQE), dark current-voltage, transmission electron microscopy (TEM) and energy dispersive X-ray analysis (EDX) will be presented.

TF-ThP22 Low-Temperature Atomic Layer Deposition of Platinum Using (Methylcyclopentadienyl)trimethylplatinum and Ozone*, **Huazhi Li**, N. Sullivan, P. Chinoy*, Arradiance

Because of the excellent electric and catalytic properties of Pt, ALD of Pt has attracted considerable attention for applications in nanoelectronics, electrochemistry, catalysis, and sensing. The most commonly applied ALD process for Pt uses (methylcyclopentadienyl)trimethylplatinum ($MeCpPtMe_3$) and O_2 as precursors. It was found that the optimum process window of this process is 250 - 300 °C[1]. Below 250 °C, very low growth rates and poor Pt nucleation on some substrates such as Si or SiO_2, are observed. These limitations rule out applications on heat sensitive polymer substrates.

To address the need for low temperature ALD Pt, processes based on ozone[2] and oxygen plasma with a subsequent reduction by H2[3] have been reported. O_3 is being used in a growing number of atomic layer deposition (ALD) processes because O_3 is a powerful oxidizer and is easier to purge than H2O, particularly at lower growth temperatures (≤ 100 °C). The development low temperature ALD processes using O_3 process[4] and low temperature plasma processes will be reported. In this work, growth kinetics, crystalline structure, resistivity, and purity of Pt thin films grown using O_3 as reactant gas in combination with the $MeCpPtMe_3$ precursor are studied. Additionally, the conformality of the $MeCpPtMe_3/O_3$ process and its nucleation behavior on a SiO_2 surface will be discussed. The results reported describe a process that is highly suited for Pt deposition on thermally fragile substrates.

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TF-ThP25 Flash Networking Poster: Surface Characterization and Luminescent Properties of Pulsed Laser Deposited Dysprosium-Doped Rare-Earth Oxyorthosilicates Thin Films*, **Martin Ntwaeaborwa**, S.N. Ogugua, H.C. Swart*, University of the Free State, South Africa

Luminescent materials or phosphors have a wide range of technological applications in electronic information displays, solid state lighting, solar cells, advertising, medical imaging, etc. Although phosphors are usually used as powders, thin films have more advantages in many practical applications. We report luminescent properties and surface states of dysprosium (Dy^{3+})-doped lanthanum gadolinium oxyorthosilicate ($La_{2-x}Gd_xSiO_5$:Dy^{3+}; where x = 0, 0.5, 1.0, 1.5, 2) that were ablation deposited onto Si (111) substrates using the pulsed laser deposition (PLD) technique. Several deposition parameters were varied, including vacuum versus partial pressure of gas (O_2 or Ar), and substrate temperature using the 266 nm Nd: YAG excimer laser. The ablated targets were prepared from powders which were synthesized by combustion method. The films exhibited tunable and white photoluminescence emission when excited by either a monochromatized xenon lamp or a 325 nm HeCd laser in air at room temperature. The PL emission colour and the peak intensity were dependent on the ratio of La to Gd, concentration of Dy^{3+}, and deposition conditions. Data from scanning electron microscopy (SEM) and atomic force microscopy (AFM) show that the major influence of the deposition conditions on the PL peak intensity was through changes in the morphology and topography of the films, which affects light scattering and out-coupling. The time-of-flight secondary ion mass spectroscopy (ToF-SIMS) was used to study the distribution of atomic and molecular ionic species on the surface of the films, while X-ray photoelectron spectroscopy (XPS) was used to analyse the chemical composition and electronic states of our samples.

TF-ThP28 Effect of a Substrate Temperature on the Properties of the RF-sputtered Indium Selenide Thin Films as a Buffer Layer for CIGS Photovoltaics, ***MyoungHan Yoo**, N.H. Kim*, Chosun University, Republic of Korea

CIGS, which has suitable optical absorption, tunable band gap, good electrothermal stability, and no toxic/hazardous pollutant, has been used in thin film solar cells with the conventional structure of glass/Mo/CIGS/buffer layer/TCO. Instead of the very noxious and polluting CdS buffer layer, Cd-free materials have been attracted great interest in the buffer layer for CIGS photovoltaic applications. The Cd-free buffer layers require some qualifications, such as a band gap energy between CIGS and TCO (typically zinc oxide, $E_g \sim 3.4$ eV), an optical transmittance ≥ 80%, and a resistivity $\leq 10^4\ \Omega\cdot$cm,[1] to replace the conventional CdS buffer layer. Indium selenides are III-VI semiconducting compounds with the wide deviation from stoichiometry, which were proposed for the Cd-free buffer layer in CIGS photovoltaics with several advantages including better heterointerface of the same elemental effusion with CIGS absorber layer. In the prior studies, indium selenides were prepared by using RF-magnetron sputtering method with $InSe_2$ target and rapid thermal annealing. The variations in film thickness, stoichiometry, annealing duration, and annealing temperature did not affect the crystallization of indium selenide precursors in amorphous nature. Subsequently, the substrate temperature, which induces significant changes in the properties of indium selenide, was varied in the RF sputtering process. Rapid thermal annealing process was performed to transform the 50-nm-thickness indium selenide into the γ-phase In_2Se_3 at 700°C for 1 min. Some analyses were examined in the structural, optical and electrical properties of the RF-sputtered indium selenide thin films with the different substrate temperatures for the optimal buffer layer in CIGS photovoltaics. [1] J. H. Yoon, W. M. Kim, J. K. Park, Y. J. Baik, T. Y. Seong and J. Jeong, Prog. Photovolt: Res. Appl. 22, 69 (2014).

TF-ThP33 Stress-curvature Relationship for Configurations with Thin and Anisotropic Substrates undergoing Large Deformations

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In a thin film configuration, the film is often stressed to conform to the surface of the substrate, commonly due to epitaxial effects, difference in thermal expansion coefficients between the film and the substrate materials, or phase transformations accompanied with volume changes. This stress causes the film-substrate system to assume a curvature. The relation that relates this curvature to the stress in the film is referred to as the Stoney equation. One of the major assumptions of the Stoney equation is that the substrate is orders of magnitude thicker than the film, leading to small and purely elastic deformation of the substrate. Moreover, the well known equation also assumes that the substrate material is isotropic in nature.

At the moment, the traditional Stoney equation is being used to relate the film stress to the system curvature. However, in majority of the cases where the film stress is measured from the system curvature, Si wafers are used as substrates. Si wafers are anisotropic in nature as they are obtained by slicing single crystals. In this paper, a more generalized version of the Stoney equation is presented.

This form of the equation is derived by first relaxing the constraints that the film is very thin compared to the substrate and that the deformations are small. Next, this formula is modified specifically for the cases of Si(001) and Si(111) wafers. Ultimately, a modified version of the Stoney equation is presented which can be used for configurations with anisotropic substrates where the thicknesses of the film and substrate are comparable, and the deformations are large. Extension of this expression to systems assuming asymmetric elliptical configurations rather than symmetric spherical deformations, is also discussed.

Keywords: Thin film, Large deformation, Stoney, Silicon, Wafer curvature

TF-ThP34 Doping of High-aspect Ratio Silicon Structures using Thin Film Dopant Sources Grown by Plasma-assisted Atomic Layer Deposition

Bodo Kalkofen, Otto von Guericke University Magdeburg, Germany*, A.A. Amusan,* Otto von Guericke University, Magdeburg, Germany*, M. Lisker,* IHP, Frankfurt (Oder), Germany*, Y.S. Kim,* Lam Research Corporation*, E.P. Burte*, Otto von Guericke University, Magdeburg, Germany

Plasma-assisted atomic layer deposition (PALD) was carried out for growing thin oxide films of silicon dopants onto flat and high-aspect ratio silicon substrates. The applicability of these films as dopant sources for shallow doping of silicon using various rapid thermal annealing methods, such as RTP, flash lamp anneal, and laser anneal, was investigated. Remote CCP and ICP sources were applied for generating oxygen radicals in the PALD processes. Tris(dimethylamido)borane was used as boron containing precursor for p type silicon doping, source layers for n type doping were grown using triethylphosphite and triethylantimony as phosphorus and antimony containing oxides, respectively.

The as-deposited films of boron oxide were highly unstable in ambient air and could be protected by capping with in-situ PALD grown antimony oxide films. Phosphorus containing films were stabilized by incorporating them into a silicon dioxide matrix by carrying out ALD processes with supercycles of phosphorus and silicon precursor reactions with oxygen radicals. Also capping of the phosphorus containing films was applied. Antimony oxide films were stable at ambient air conditions. Conformal growth of such films could be obtained on silicon trench structures of 6:1 to 10:1 aspect ratio with pitch below 50 nm.

Boron and phosphorus doping of silicon could be obtained using the respective oxide films as dopant sources. This was confirmed by SIMS and sheet resistance measurements. Diffusion of antimony into silicon from antimony oxide needs to be further improved by optimizing the annealing conditions. The influence of source layer thickness and different annealing conditions during rapid thermal annealing processes on the doping results was investigated. Controlled doping of 3-D nanostructured devices by pre-deposition with ALD source layers should be feasible by this method.

TF-ThP36 Kurt J. Lesker- TORUS "Mag Keeper" Sputtering Sources- "Enabling Thin Film Coating Technology for a Better World"

Jason Hrebik, Kurt J. Lesker Company

The thin film coating industry, particularly in magnetron sputtering, is a critical means for our current and future advancements in technology. There are a wide range of applications, which have many critical performance requirements to make them successful. The main component driving these applications is the magnetron sputtering cathode or "magnetron".

In many cases, it is difficult to find an ideal "magnetron" that can meet all of the process requirements. In addition, there are a broad range of "magnetron" providers in the industry that all have advantages and disadvantages to their technology. This can make choosing the best option very difficult.

One of the most critical performance requirements in any magnetron design is target cooling. Good thermal conductivity between the target and the cathode is essential for maximum power density and sputtering rate. The new Mag Keeper sputtering source utilizes an enhanced target cooling design in which the cooling water flows through a brazed copper channel that is in direct contact with the backside of the sputtering target. This along with a magnetically enhanced clamping force provides an uncompromised cooling advantage.

In addition, the Mag Keeper design has only a single metal seal, contains no O-rings, and utilizes all ceramic insulators, making it both HV and UHV compatible.

Over the course of extensive performance testing campaign, the design showed several key advantages. Using a variety of target materials, it was found that the Mag Keeper's cooling efficiency is comparable to that of a direct-cooled magnetron providing the ability to run at power densities over 200 watts/ in2 with thermally conductive materials such as copper and aluminum. A key advantage to the magnetic profile was the ability to operate a 0.375" thick non-magnetic target at 0.5mTorr pressure. In terms of target erosion, the Mag Keeper design has a very broad profile maximizing both utilization and uniformity. In addition, with the High Strength magnet configuration, a 3" source was able to sputter up to 3mm thick Fe.

From a mechanical standpoint, the Mag Keeper source does not use a target clamp or anode shield assembly resulting in a very quick target change averaging less than 5 minutes due to only having to loosen (2) bolts in order to access the target.

In conclusion, the Mag Keeper magnetron design offers the industry a design that is capable of meeting a very broad range of application requirements with the conveniences needed for meeting production efficiencies!

TF-ThP39 Femtosecond X-Ray Magnetic Circular Dichroism Spectroscopy at an X-Ray Free Electron Laser

Daniel Higley*, K. Hirsch, E. Yuan, E. Jal, G.L. Dakovski, A.A. Lutman, J. MacArthur, A.H. Reid, T. Liu,* SLAC National Accelerator Laboratory*, J. Joseph,* Lawrence Berkeley National Laboratory*, A. Tsukamoto,* Nihon University*, H.A. Durr, W.F. Schlotter*, SLAC National Accelerator Laboratory

In the last twenty years, the field of ultrafast magnetization dynamics has seen tremendous growth and development. Ferromagnetic transition metals have been seen to demagnetize on a sub-picosecond time-scale when excited by ultrafast laser pulses, much faster than expected from dynamics close to equilibrium. The mechanism of this ultrafast magnetization quenching, almost twenty years after its discovery, is still a matter of active debate. Other materials exhibit ultrafast switching of the magnetization when excited similarly. The switching mechanism, however, is also still debated. To unravel the mysteries of these processes requires probes which can sensitively and reliably probe the transfer of angular momentum and energy between the electronic, electronic spin, and lattice systems.

X-ray magnetic circular dichroism spectroscopy (XMCD) directly and element-specifically probes the spin and orbital magnetic moments of electrons in matter and has proven invaluable in studies of static magnetism. This information is extracted from the difference in absorption of right- and left-circularly polarized x-rays at spin-orbit split resonances where core-level electrons are excited into unoccupied valence states.

XMCD with femtosecond time resolution is an ideal tool to investigate ultrafast magnetization dynamics. Femtoslicing beamlines at synchrotrons have been used to perform such measurements and make seminal contributions to the field of ultrafast magnetization dynamics. The low photon throughput of these sources, however, necessitates long integration times for measurements and restricts the possibility of systematic studies as well as measurement of small signals. X-Ray Free Electron Lasers (XFELs), which provide femtosecond pulses with a much increased flux compared to femtoslicing sources, give an important path to extending these results.

Here, we report on ultrafast XMCD spectroscopy measurements in the soft x-ray range at an XFEL utilizing a recently installed variable polarization undulator at the XFEL LCLS at the SLAC National Accelerator Laboratory. We are able to record static XMCD spectra of GdFeCo samples over the iron L-edges and gadolinium M5 edge which match those observed at synchrotrons. In addition, by monitoring the time-resolved XMCD at these edges we reproduce the classic observation of a transient ferromagnetic alignment of antiferromagnetically coupled spins in amorphous GdFeCo during ultrafast, laser-induced, switching. With the high-flux and intrinsically ultrafast pulses of XFELs, we are able to record this measurement in less than an hour, a fraction of the time required for the original measurement.

Tribology Focus Topic
Room: Hall 3 - Session TR-ThP

Tribology Poster Session

TR-ThP1 Adhesion of Hard Coating on Neutral Nitrided Tool Steel Surfaces, *P. Abraha,* Meijo University, Japan*,* ***Takuma Matsuda***, Meijo UnUniversity, Japan

Hard thin films such as titanium nitride and titanium aluminum nitride films are widely used to improve the durability of cutting tools, punches, and dies that are extensively used in the manufacturing industries. In general, the hardness of hard coating films is about three to five times that of tool steel surfaces causing a remarkably high stress that would eventually lead to the detachment of the hard coating. One way of improving the adhesion of hard coatings is to increase the surface hardness of the tool steel, narrowing the gap, to maintain a reasonably stronger bondage.

In this research, neutral nitriding operation was performed on the SKH 51 tool steel surface before TiAlN coating. Neutral nitriding is a plasma process that allows only the neutral species to diffuse into the interstitial layer of the tool steel surface. The process delimits the formation of the undesirable brittle compound layer to a much higher treatment time while keeping the as-finished surface conditions. The scratch test was performed to provide a measure of coating/tool steel adhesion.

The results of our experiments show that in nitriding SKH 51 tool steel for 6 hours, the hardness of the tool steel surface was increased by about two times, 1400 Hv compared to the untreated sample (750 Hv). The scratch tests show that a well-defined failure of the coating occur at a higher critical load in tool steel samples that are neutral nitrided compared to samples without the pre-treatment. Our results demonstrate that neutral species based nitriding is effective for high adhesion of hard coating materials on tool steel surfaces.

TR-ThP2 Neutral Nitriding of Austenite Stainless Steel at Low Temperature*,* ***Jun Tamura****, P. Abraha*, Meijo University, Japan

Stainless steels have very good corrosion resistance but the lower surface hardness poses marked limitation on the range of tribological applications that can be envisaged. Here plasma nitriding treatment was performed to improve the hardness without altering the corrosion resistance of austenitic AISI 304 stainless steels.

In nitriding the AISI 304 stainless steel, the passive Cr_2O_3 layer that protects the surface from corrosion is removed first as it hinders the diffusion of nitrogen species into the bulk of the stainless steel material. The removal of the passive layer was done by argon sputtering and the subsequent nitriding was performed in electron beam excited plasma apparatus under nitrogen and hydrogen atmosphere. The sample temperature was controlled at 400, 450, and 500 degree centigrade. Treated and untreated samples were characterized by means of morphological analysis, Vickers hardness measurements, optical microscope, and x-ray diffractometry.

The results of our experiments show that in neutral nitriding of stainless steel under low temperature, 400 degrees centigrade, the surface hardness increased to 780 Hv, more than two times, that of the untreated surface. Moreover, the cross sectional images show clear nitrogen expanded austenite layer without the formation of compound layer. Measurements of surface roughness and conditions of the surfaces were reasonably maintained. The above results indicate that stainless steels can be used as sliding or meshing mechanical parts in environments such as vacuum chambers and underwater machinery.

TR-ThP3 Non-Oxidized Metallic Transfer Film Formation Originated from Metallic Nanoparticles Embedded in Diamond-like Carbon under Sliding in Air*,* ***Takanori Takeno****, H. Miki, T. Takagi, K. Adachi*, Tohoku University, Japan

This study clarifies the formation mechanisms of thin layer on the counter material when nanocompsite coatings consisted of nanoparticles and diamond-like carbon were sliding against steel ball in air. When low friction was obtained in such combination, thin metallic film was formed on the counter material. What we could find is that such metallic film does not contain oxygen less than the one coming from native oxidized surface.

Hybrid deposition system composed of CVD and PVD sources allows us to make nanocomposite structure based on diamond-like carbon (DLC) coatings. Thanks to magnetron sputtering system, target material in sputtering source is extracted as a form of nanoparticle, and its size varies depending on deposition condition and type of material. During sputtering process, hydrocarbon plasma is generated, and hydrogenated amorphous carbon phase is formed. Typical structure of the composite coatings is that nanometer-sized metallic particles are well dispersed in amorphous carbon host matrix. Friction tests are conducted under vacuum or dry conditions. Various analytical techniques including transmission electron microscope (TEM), secondary ion mass spectrometer (SIMS), Raman spectroscopy, Scanning Electron Microscope equipped with energy dispersive X-ray spectrometer (SEM-EDS), X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES).

Once iridium was selected as an inclusions in diamond-like carbon host matrix, Ir-containing DLC showed friction coefficient of less than 0.1 despite friction coefficients of Ir and DLC showed ~ 0.3. In-situ electrical contact resistance measurements revealed that such coating provides not only low friction coefficient but also low electrical contact resistance, several tens ohms. When low friction and electrical contact resistance was achieved, metallic thin film was formed on the counter material. EDS analyses revealed that chief material forming the metallic film is Ir. It could be understood that nanoparticles formed metallic thin film on the counter materials during friction. It is worth noting that such transfer film does not contain oxygen even friction tests were conducted under air. Same phenomena could be observed with Cu- and Ag-containing DLCs. Even for both cases, metallic transfer films were formed during friction tests, and we could not detect oxygen from the transfer by EDS. Possibly, tribochemical reaction occurred and oxygen from air reacts to carbon in DLC, then gas phase or wear particles of carbon-oxides were formed. Details on a possible chemical reaction between the coatings and air will be discussed at the conference.

TR-ThP4 Achieving Very Low Friction with Molybdenum Disulfide Nanoparticles Embedded into Hydrogenated Amorphous Carbon Coatings*,* ***Kazuki Ikoma****, K. Adachi, T. Takeno*, Tohoku University, Japan

Solid lubricants are usually used at severe environment (ex. vacuum). Among these lubricants, MoS_2 is widely used for many mechanical systems and shows low friction by forming transferred layer with MoS_2 lamellar structure. However, one of the drawbacks of MoS_2 is that it must be kept in dry nitrogen condition to avoid oxidation of molybdenum-disulfide.

We have proposed amorphous carbon coatings containing Molybdenum disulfide (MoS_2-DLC) as a new solid lubricant. It is well known that amorphous carbon coating is used for a gas barrier coating decreasing gas permeability. So, we have made the coatings with nanocomposite structure that MoS_2 clusters with several nm in diameter are embedded in hydrogenated amorphous carbon (a-C:H) host matrix. It was reported that friction coefficient obtained by MoS_2 sliding against SiC ball decreased with increasing MoS_2 concentration It is worth noting that MoS_2-DLC with proper MoS_2 concentration showed lower friction than MoS_2 coatings. Further reduction of friction could be obtained by changing a deposition parameter leading to a modification of host matrix of amorphous carbon. Therefore, not only concentration of MoS_2 but also properties of amorphous carbon host matrix are very important for achieving low friction.

This study focuses on hydrogenated amorphous carbon host matrix to achieve low friction. Especially, deposition parameter that controls properties of carbon host matrix was changed to produce various amorphous hydrogenated carbon host matrix containing MoS_2 nano-clusters. After the friction tests, a thin transferred layer proving low friction is well analyzed by various analytical techniques including transmission electron microscope (TEM), secondary ion mass spectrometer (SIMS) and Auger electron spectroscopy (AES). It was clarified that thin transferred layer was composed of two phases. Dominant one contains mainly MoS_2 with lamellar structure. It is worth noting that there is very thin carbon-rich layer with ~ 5 nm between MoS_2-rich layer and the counter material of SiC, and carbon at thin carbon layer comes from carbon host matrix. Taking into account the selective transfer of carbon from the coating and the possibility that such carbon-rich layer becomes a kind of support for forming lubricious MoS_2 layer, friction properties could be controlled by the properties of carbon. In this study, formation mechanisms of such two-phase thin layer are clarified, first. Then, we try to achieve very low friction with low MoS_2 concentration with optimized phase of carbon phase in the coating. Finally, design guideline for achieving low friction utilizing MoS_2-DLC coatings is proposed.

TR-ThP5 Study of Wear-corrosion Mechanisms of CoCrMo Alloys Alone and Coated with TiAlN Coatings, ***Martin Flores***, *O. Jimenez,* Universidad de Guadalajara, Mexico*, E. Andrade*, Universidad Nacional Autonoma de México

The wear-corrosion phenomenon is present in biomedical alloys that are used in artificial implants to replace natural joints. This damage limit the service life of such implants, the hard coatings can improve the resistance to wear and corrosion. The coatings of TiAlN were deposited on CoCrMo alloys by magnetron sputtering. In this work we study the wear mechanism of the samples coated and alone in a simulated body fluid with an ion concentration similar to that in the human blood. The structure of coatings was studied by means of XRD and the composition by RBS and EDS techniques. The tribocorrosion behavior of CoCrMo alloys alone and coated with TiAlN coatings was studied in simulated body fluid. The tribocorrosion was performed using a ball on plate reciprocating tribometer, the tests were conducted at 37 °C of temperature. The loads used were between 0.5 N to 2N, the oscillating frequencies was 1Hz. The corrosion and tribocorrosion were studied using open circuit potential (OCP) and potentiodynamic polarizations. In order to study the wear mechanisms, the debris, the topography and composition of worn surfaces were analyzed by means of SEM and Raman spectrocopy. The coatings improve the corrosion and tribocorrosion resistance of CoCrMo alloys and change the wear mechanisms of the substrate.

TR-ThP6 Frictional Property Optimization of Metal Oxide Thin Films by a Combinatorial Optimization of Crystal Orientation for Tribology (COCOT) Technique, ***Michiko Sasaki***, *M. Goto, A. Kasahara, M. Tosa*, National Institute for Materials Science, Japan

Combinatorial technology has much attention as the effective method for the development of novel functional materials. Also, the combinatorial technique have been used as one of the analysis methods in tribology research.

In this study, we were performed crystal structure analysis by combinatorial optimization of crystal orientation for tribology (COCOT) technique at the sliding surface of after the friction measurement (while changing the load continuously) of metal oxide thin film such as ZnO and Cr_2O_3.

As a result, it is a correlation in the crystal optimization of the sliding surface and the counter ball materials had an effect on the friction coefficient of the thin films.

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 $Mo_xW_{1-x}Te_2$ 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)

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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

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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 MoS_2 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 $OH^{\cdot}$. 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, MoS_2 nanosheets and nanoparticles. However, detection of free radicals at cellular level is still a challenge.

In this attempt, layered molybdenum disulfide (MoS_2) were synthesized via hydrothermal method. SBA-15 polymer template were utilized during hydrothermal process to grow MoS_2 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 MoS_2 crystal. Wet chemical exfoliation of MoS_2 were carried out in aqueous solution of Pluronic$^{\grave{O}}$ F-127 having hydrophobic and hydrophilic chains. Pluronic$^{\grave{O}}$ F-127 was used to bring down the buoyant density of MoS_2. 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 MoS_2 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 MoS_2, 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 MoS_2 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 MoS_2, 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 MoS_2, indicating stronger interactions, and (3) the barriers for forming intermediate species in alcohol synthesis process reduce significantly in comparison to that on unsupported MoS_2. On the basis of these energetics, we conclude the Cu(111) substrate promotes methanol synthesis from syn gas on single-layer MoS_2 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).

*This work is supported in part by the U.S. Department of Energy under grant DE-FG02-07ER15842

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.

Research supported by DOE.

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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.

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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_3O_4 core-shell particles for medical applications.

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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.

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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_2ZnSnS_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$_2$ZnSn$_{(1-x)}$(IV)$_x$S$_4$ by means of this processing approach will be reported.

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Plasma Science and Technology
Room: 210A - Session PS+SE-FrM

Atmospheric Pressure Plasma Processing II

Moderator: Souvik Ghosh, Case Western Reserve University

9:00am **PS+SE-FrM3 Scaling Atmospheric Pressure Plasma Sources for Manufacturing-Scale Applications**, ***Steven Shannon***, North Carolina State University **INVITED**

Material processing using plasmas at atmospheric pressure presents one of the great areas of future growth for the Plasma Science and Technology Division of the AVS. Extension of plasma processing to atmospheric pressures (and ironically eliminating the need for "vacuum") provides two key advantages in processing. The first is the reduced cost and increased throughput that could be realized in equipment that does not require high vacuum design, load locks, etc. The second, and more significant, are the new applications that plasma science can now contribute to including water treatment, soft materials processing, processing of non-vacuum-friendly materials, and medicine.

Atmospheric plasma systems for manufacturing have the same high volume integration challenges that low pressure plasma systems do. These are scalability and throughput. These systems need to be able to process large areas (or volumes, depending on the application). This throughput scaling presents a challenge especially when some level of homogeneity in process both within a sample and from sample to sample are required. Maintaining this process uniformity over a large area is further complicated by the need to maintain a high rate of reactive specie production, especially when the standard solution of "turn up the power" results in typically undesirable instability and heating in these higher pressure discharges.

At NCSU, researchers have developed an atmospheric plasma source that seeks to address these scale-up concerns of size and reactant production. This coaxially driven source can be driven in the VHF range of frequencies (60MHz - 200MHz, with 162MHz used in the work shown here) with a plurality of feed gases not requiring noble gas dilution. The VHF heating combined with source circuit design produce a volume glow with power densities ranging from 1W/cm^3 to 20W/cm^3. The unique source design enables operation of an RF driven / DC grounded electrode that enables delivery of gas and liquid precursors through the electrode surface. This enables the introduction of liquid precursors into the active plasma region while maintaining a stable volume glow. Multiple sources can be run in parallel for larger volume operation, and scalability has been demonstrated. Reactive specie production has been quantified for air plasmas and water plasmas (with water delivery from the powered electrode). The water electrode configuration yields OH concentrations over 10^{15}/cm^3 in the active plasma region.

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This work is supported by the NSF I/UCRC program through the Center for Lasers and Plasmas in Advanced Manufacturing, the NCSU Chancellor's Innovation Fund, and Advanced Energy Inc.

9:40am **PS+SE-FrM5 Improving of Harvest Period and Crop Yield of *Arabidopsis Thaliana L.* using Nonthermal Atmospheric Air Plasma**, ***Kazunori Koga***, *T. Sarinont, T. Amano, H. Seo, N. Itagaki, M. Shiratani*, Kyushu University, Japan

Nonthermal atmospheric plasmas have been widely used for biomedical applications [1-3]. Growth enhancement of plants is one of the important applications of such plasmas. Here we have studied effects of atmospheric air plasma irradiation to seeds of *Arabidopsis thaliana L.* on the harvest period and crop yield. Experiments were carried out using a scalable DBD device [2, 3]. The device consisted of 20 electrodes of a stainless rod of 1 mm in outer diameter and 60 mm in length covered with a ceramic tube of 2 mm in outer diameter. The discharge voltage and current were 9.2 kV and 0.2 A. 20 seeds of *Arabidopsis thaliana L.* were set 3 mm below the electrodes. After 3 minutes plasma irradiation, they were grown on rockwool until the harvest stage. The harvest period is defined as time from the beginning of cultivation to the first seed production. To evaluate the growth enhancement ability of the plasma irradiation, the area of two primary leaves of eight plants, namely 16 leaves, was measured every three days. The whole experiment was repeated 3 times with similar results. Data were analyzed by two-way analysis of variance. The harvest period without and with plasma irradiation are 71.31±5.63 and 66.53±3.82 days. The seed weight without and with plasma irradiation are 0.0201±0.0024, 0.0225±0.0016 mg/seed. The leaf area after 28 days from the beginning of cultivation without and with plasma irradiation are 0.049±0.011 cm^2 and 0.064±0.014 cm^2. These measured values without and with plasma irradiation are statistically significance different at $\alpha = 0.05$ ($P < 0.05$). Plasma irradiation brings about 7% shorter harvest period, 12% higher seed weights and 30% larger primary leaves, compared to those without plasma irradiation. Thus, plasma irradiation to seeds is a cost effective and environmental friendly method for improving of harvest period and crop yield of plants. The growth enhancement mechanism will be discussed in the presentation.

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10:00am **PS+SE-FrM6 Numerical Modelling of Atmospheric Pulsed Streamers over Water; Electrodynamics at the Interface**, ***Alex Lindsay***, *S. Shannon*, North Carolina State University, *D.B. Graves*, University of California at Berkeley

There is significant interest in characterizing interactions between atmospheric plasmas and water for applications in medicine, water decontamination, distributed farming, etc. In one particular example members of the community are investigating replacement of invasive electroporation for drug delivery and gene therapy with low-power atmospheric plasma devices. Although the mechanism by which electric fields create conductive pathways for drug delivery into cells is generally known, the mechanism by which plasmas create those liquid-phase electric fields is an active area of research. Pioneering work in [1] has done much to advance our understanding, but more work remains. We wish to present modeling tools that are open to the community in the hope that this will enhance development of the tools, scrutiny and reproducibility of numerical results, and the pace at which plasma-liquid research is conducted. By developing open community tools, we hope to reduce the time-waste that comes from different groups re-inventing the wheel to study similar phenomena. With those motivations, we consider both finite-volume and finite-element discretizations of the Poisson and continuity equations governing electrodynamics in the gas and liquid phases. For a first pass, a local-field approximation is used to study streamer propagation in a point-to-plane configuration with water serving as the planar electrode. Different methods for stabilization (e.g. inconsistent vs. consistent, streamline and/or crosswind) as well as markers for mesh adaption (potential, electron density curvatures) are considered.

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10:20am **PS+SE-FrM7 Application of Atmospheric Pressure Plasma treatment on Carbon Fiber Reinforced Plastics for Adhesive Bonding**, ***Timo Hofmann***, *J. Schäfer,* Bundeswehr Research Institute for Material, Fuels and Lubricants, Germany*, T. Löbel,* German Aerospace Center (DLR)*, T. Meer,* Airbus Group Innovations*, J. Rehbein, J. Holtmannspötter*, Bundeswehr Research Institute for Material, Fuels and Lubricants, Germany

The demand for environmentally friendly means of transportation has led to a strong increase in the use of carbon fiber reinforced plastics (CFRPs). Joining of CFRP structures is currently performed using rivets and bolts. In order to exploit further weight-saving potential, the usage of adhesive bonding is investigated.

An important key factor for the success of adhesive bonding is the surface pre-treatment of the adherents. In this contribution, CFRP surfaces were treated using Atmospheric pressure plasma jet (APPJ) as a method to clean the samples and to improve adhesion by creating surface functional groups.

We present a detailed investigation of the surface morphology and the composition of CFRPs before and after treatment with APPJ. The CFRP surfaces were examined using a combination of Field-Emission Scanning Electron Microscopy (FE-SEM), Atomic Force Microscopy (AFM), Energy-Dispersive X-ray spectroscopy (EDX), and X-Ray Photoelectron Spectroscopy (XPS). Destructive tests were carried out to determine the adhesive strength and the failure mode as a function of APPJ.

We demonstrate that APPJ-processes can be used to form structural and long term stable bonds. Our results show that through the combination of analytical techniques and destructive tests it is possible to develop an understanding of the processes at the surface and to optimize the plasma treatment process.

10:40am **PS+SE-FrM8 Atmospheric Plasma Deposition of Transparent Organosilicate Multifunctional Coatings on Plastics in Air**, ***Siming Dong***, *Z. Zhao, R.H. Dauskardt*, Stanford University

Atmospheric plasma deposition is a versatile coating process that enables deposition on large and/or complex shapes in air. The low temperature plasma and solvent free process allows deposition on, and simultaneous functionalization of plastic substrates in a single step. Building on our previous studies, we demonstrate a highly efficient deposition method using two precursors, an inorganic tetraethoxysilane (TEOS) and an organic 1, 5-cyclooctadiene (CYC), to deposit multi-layer organosilicate transparent coatings on poly methyl methacrylate (PMMA) and silicon (Si) substrates with atmospheric plasma deposition in air. The coatings deposition rate, transparency, chemical composition and adhesion with the PMMA substrate were investigated. Using only the TEOS precursor, high density and elastic modulus coatings were deposited on PMMA but with poor adhesion. The addition of the organic CYC precursor allowed controlled incorporation of organic components into the coating molecular network which significantly improved adhesion. The deposition rate increased from ~65 nm/min for the single precursor to ~130 nm/min for the two precursor process. The coatings exhibited ~100% transmittance in the visible wavelength range. FTIR and Raman spectroscopy of the coatings showed that the organic component $(\text{-C-C-})_n$ in the coatings can be incorporated to form an organosilicate molecular network. This incorporation increased the coating deposition rate and also resulted in mechanical plasticity in the coatings. The adhesion of coatings with PMMA increased from ~2 J/m^2 to ~10 J/m^2 and the Young's modulus ranged from 22GPa to 34GPa. Coatings structures including composition and coating thickness to achieve optimized hardness and adhesive properties are reported.

11:00am **PS+SE-FrM9 Atmospheric Plasma Deposition of Anti-Reflection Coatings on Silicon in Open Air**, ***Michael Hovish***, *R.H. Dauskardt*, Stanford University

For many modern energy and sensing applications, multilayer optical coatings are an effective way to dramatically improve light collection. Traditionally, such multilayer coatings are deposited on hard substrates using vacuum depositions. Furthermore, traditional vacuum techniques are not easily scalable, due to high costs and poor integration into the manufacturing scheme. Atmospheric plasma deposition has received attention in materials processing due to the ability to deposit functional coatings at room temperature and in open air. Room temperature operation allows for a dynamic range of substrates, both organic and inorganic. In addition to these qualities, atmospheric plasma deposition is a solvent free technique, making it a competitive alternative to sol-gel methods. In our research program, we have successfully shown several material systems which are amenable to atmospheric plasma deposition, including multifunctional organosilicate and metal oxide films. In particular, the solvent-free deposition of metal oxide films at atmospheric pressure and near room temperature provides an attractive platform for the design and fabrication of optical coatings.

We have employed atmospheric plasma to deposit thin, anti-reflection coatings on silicon. Both TaO_x and TiO_x films were investigated as candidates for single layer anti-reflection coatings. Films were optimized for low reflection within the visible wavelengths of light. High purity helium gas was used to transport either tantalum ethoxide or titanium ethoxide vapor into the afterglow of a helium-nitrogen plasma. A high temperature precursor delivery system was used to prevent the condensation of precursor vapors en route to the afterglow. Within the afterglow, the metal-organic compounds undergo molecular fragmentation and redistribution onto the substrate. Deposition rates, chemical compositions, optical properties, and adhesion energies to the substrate were investigated as a function of plasma power and gas composition. Spectral reflectance at 10° from normal was measured to determine the anti-reflection properties of the coatings. Atmospheric plasma deposited films on silicon show excellent anti-reflection properties, with less than 3% reflection loss near 550 nm.

11:20am **PS+SE-FrM10 Polymer Thin Film Deposition using Atmospheric Pressure Single Plasma Jet or Plasma Jet Array from a Plasma Gun Device***,* ***Céline Vivien****,* IEMN CNRS/Université Lille 1, France*, E. Robert, J.-M. Pouvesle*, GREMI CNRS/Université d'Orléans, France

Plasma Enhanced Chemical Vapour Deposition (PECVD) processes have been used for decades for surface processing in a wide range of industrial applications like semiconductor films, low-k films, barrier diffusion. Thin film deposition is especially of high interest for biomedical applications for the production of protective coatings, adhesion layers, hydrophilic or hydrophobic layers. Up to now, most of used processes are usually realized under low pressure. Actually, there is a great and increasing interest in the development of plasma sources operating at atmospheric pressure. The present work deals with plasma polymerisation of TMDSO and HMDSO with a Dielectric Barrier Discharge plasma jet at atmospheric pressure, the Plasma Gun developed in GREMI. Depending on parameters like voltage, frequency, carrier gas and monomer injection, the deposited polymer appears either as a gel-like coating or a transparent film with fringes. Deposits are characterized by Fourier Transformed IRspectroscopy and contact angle measurements. The precursor used was introduced in both liquid or gaseous state, in case TMDSO and only gaseous state in case of HMDSO. The liquid flow rate was regulated by a peristaltic pump (Ismatec) while the vapour flow was ensured by bubbling nitrogen or oxygen with a fixed flow rate of 10 sccm. Microscope slides and polished Silicon wafer (100) were used as substrates. The polymerized coatings have been obtained at frequencies between 500Hz and 4 kHz, for applied voltages between 14 and 20 kV and exposure times from 1 to 10 minutes. The deposition were realized with plasma tube edge-to-substrate distances ranging from 3 to 12 mm. Profilometer measurements revealed thicknesses comprised between 500 nm and 1.5 µm at the middle of the deposit. Deposited films analyses clearly show the efficiency of this atmospheric plasma-type TMDSO and HMDSO polymerisation and their similarity with those usually realized under low pressure RPECVD. The most interesting deposited films are obtained when the monomer is introduced under gaseous state, the samples clearly showing a better homogeneity. The influence of the transport gas is not evidenced. More experiments and analyses need to be achieved to complete these preliminary results. It must be stressed that multi-spot deposition has been obtained from plasma multi-jet delivered by a single Plasma Gun.

11:40am **PS+SE-FrM11 XPS to Investigating Spatial and Temporal Modification of Polymeric Platforms for Micro-Fluidic Devices**, ***Marshal Dhayal***, CSIR Centre for Cellular and Molecular Biology (CCMB), India

Spatial and temporal changes in surface chemical composition silicon (Si), carbon (C) and oxygen (O) of polydimethyl siloxane surfaces before and after plasma treatment were estimated from quantitative elemental analysis of X-ray photoelectron spectroscopy (XPS) wide scan spectra. Theoretical ratio of Si/C/O in repeating unit $(\text{–}[\text{Si-}(\text{CH}_3)_2\text{-O}]_n\text{–})$ of polydimethyl siloxane were calculated and were compared to experimentally obtained ratio for Si/C/O obtained from untreated and plasma treated surfaces used for micro-fluidic devices. The contact angle measurements have shown that surfaces treated by air plasma can recover up to about 50% of its hydrophobic nature in less than 30 min of air exposure. These plasma modified surfaces were functionalized with poly(ethylene glycol) (PEG) silane to obtained polydimethyl siloxane surface as hydrophilic in nature for micro fluidic application. The surface chemistry of PEG-functionalized polydimethyl siloxane substrate has been studied using XPS. These different types of surfaces were used fabricate micro-fluidic devices and effects of surface nature of micro channels on fluid velocity were observed in PEG grafted micro channel in polydimethyl siloxane base micro fluidic devices. The effect of different pH of the fluids on the fluid velocity in polydimethyl siloxane -based micro channel was also studied.

Plasma Science and Technology
Room: 210B - Session PS+SS+TF-FrM

Atomic Layer Etching (ALE) and Low-Damage Processes II
Moderator: Toshihisa Nozawa, Tokyo Electron Ltd.

8:20am **PS+SS+TF-FrM1 Atomic Layer Etching of Silicon Dioxide to Enable Self-aligned Contact Integration**, *B. Finch, H. Singh, **Eric Hudson***, Lam Research Corporation **INVITED**

CMOS devices have continued to scale dimensionally following the implementation of FinFET transistors. Self-alignment of the source and drain contact to the gate has been presented as an integration solution starting at the 22nm technology node[1]. This self-aligned contact (SAC) integration creates additional challenges and constraints on the etch process for the 10 nm node and beyond. Due to smaller feature dimensions, lithography overlay, and full contact wrap-around of the transistor fins, unprecedented etch precision is now required.

A novel approach for SAC oxide etching has been developed which addresses the many tradeoffs of this application using a directional atomic layer etch process (ALE) as reported by Hudson et al[2]. Key trade-offs to enable contact etching capability of CDs as small as 10 nm include SAC spacer loss, lack of profile control, and contact not-opens. This cyclic SiO_2 ALE process repeats discrete unit process steps of fluorocarbon deposition and ion bombardment to achieve high selectivity of SiO_2 to Si_3N_4 while simultaneously addressing these tradeoffs. Oxide removal rates can be precisely controlled with minimal removal of Si_3N_4 films, enabling a highly selective etch process. Anisotropic, directional etch behavior superior to traditional SiO2 etch is enabled, creating vertical oxide profiles. This capability is highly desirable for SAC etch applications as it maintains the integrity of the gate electrode spacer during etch. Experimental results showing the ability of this oxide ALE process to eliminate tradeoffs is presented

[1] C. Auth, et al, "A 22 nm high performance and low-power CMOS technology featuring fully-depleted tri-gate transistors, self-aligned contacts and high density MIM capacitors," accepted in VLSI Symp. Tech. Dig., Jun. 2012.

[2] E. Hudson, et al, "Highly Selective Atomic Layer Etching of Silicon Dioxide Using Fluorocarbons," accepted in AVS 61st International Symp. & Exhibition, Nov. 2014.

9:00am **PS+SS+TF-FrM3 High Performance Self Align Contact Etching with Newly developed Quasi-ALE**, ***Akihiro Tsuji***, Tokyo Electron Miyagi Limited, Japan, *M. Tabata, H. Watanabe, T. Katsunuma*, Tokyo Electron Miyagi Limited, *M. Honda*, Tokyo Electron Miyagi Limited, Japan

The Self-Aligned Contact (SAC) process has been widely adopted to achieve aligned narrow contacts between electrodes as the pitch shrinkage has progressed with the miniaturization of devices in high-scale integration. In SAC fabrication, it is important to achieve high selectivity of the interlayer insulator (SiO_2) over an etch stop film (SiN) to improve insulation tolerance between the contact plug and the wiring. Such high-selective etch processes have been realized by depositing fluorocarbon (FC) film selectively on the SiN film by using the composition difference between SiO_2 and SiN with fluorocarbon plasma, which protects SiN surface during SiO_2 etch. In order to minimize SiN loss, a balance of FC film thickness and the penetration depth of the ion energy on SiN become significant [1,2]. When trying to achieve improved SiN loss reduction, reducing ion energy is one effective solution, but a balance of ion energy flux and FC radical flux ($E_i \Gamma_i / \Gamma_{CF}$) breaks down, resulting in an excess amount of deposition, causing etch stop to occur. This is caused by the limited control margin of the ion energy flux over the FC radical flux ratio using conventional processes.

Atomic Layer Etching (ALE) concept has attracted great attention in recent years for its precise fabrication potential at the atomic level and its ability to solve this issue [3,4]. ALE method enables clear separation of ion energy flux and FC radical flux supply by controlling $E_i \Gamma_i / \Gamma_{CF}$ dynamically using a new parameter of flux ratio respective to step time. Furthermore, specific control of the surface condition at each cycle is expected to be effective for precise fabrication. This report discusses the application of the ALE concept in the SAC process as a Quasi-ALE scheme with consideration for implementation to volume production. This scheme realized a dramatic improvement of SiO_2 etch performance with substantial reduction of SiN loss. Further analysis of the surface condition by XPS, SIMS, HR-RBS helped determine the mechanism of selectivity enhancement. Quasi-ALE technology is a promising weapon, corresponding to leading-edge processes of various fabrication requirements along with the miniaturization of devices, towards 10nm and beyond.

Reference

[1] T.Tatsumi, M.Sekine et al. JVST B 18(4), 2000

[2] M.Matsui, M.Sekine et al. JVST A 19(4), 2001

[3] D.Metzler, G.S.Oehrlein et al. JVST A 32(2), 2014

[4] M. Honda, AVS 61th Int. Symp. & Exhibit. (2014)

9:20am **PS+SS+TF-FrM4 Fluorocarbon Based Atomic Layer Etching of Si_3N_4 and Selectivity of SiO_2 over Si_3N_4**, ***Chen Li***, *D. Metzler, G.S. Oehrlein*, University of Maryland, College Park, *C.S. Lai, M. Danek, E.A. Hudson, A. Dulkin*, Lam Research Corporation

Angstrom-level plasma etching precision is required by semiconductor manufacturing for the sub-14 nm technology node. Atomic layer etching (ALE), achieved by a series of self-limiting cycles, can precisely control the amount of reactant available and resulting etching depths. Recently, controlled etching of SiO_2 at the Angstrom-level based on steady-state Ar plasma, periodic injection of a defined number of fluorocarbon (FC) molecules, and synchronized plasma-based Ar^+ ion bombardment has been demonstrated [1,2]. This novel ALE approach is achieved by deposition of a thin (several Angstroms) reactive FC layer on the material surface using pulsed FC flow. Subsequent low energy Ar^+ ion bombardment removes the FC layer along with SiO_2 from the surface. The ion energies were selected to allow only chemical enhanced etching to take place without any physical sputtering, which enables a self-limited SiO_2 removal. We report on controlled etching of Si_3N_4 and SiO_2 layers of the order of one to several Angstroms using this cyclic ALE approach. The work was performed in an inductively coupled plasma reactor. Using SiO_2-Si_3N_4-SiO_2 multi-layer stacks on a Si substrate enabled precise evaluation of selectivity, self-limitation, and modification by *in situ* real time ellipsometry. Si_3N_4 etching and etch selectivity of SiO_2 over Si_3N_4 were studied and evaluated with regard to the dependence on FC surface coverage, precursor selection, ion energy, and etch step length. Surface chemistries of SiO_2 and Si_3N_4 were investigated by vacuum transferred x-ray photoemission spectroscopy (XPS) at each stage of the ALE process. The choice of precursor can have a significant impact on the surface chemistry and therefore the chemically enhanced etching characteristics.

The authors gratefully acknowledge financial support of this work from National Science Foundation (CBET-1134273) and Lam Research Corporation.

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[2] E. Hudson, V. Vidyarthi, R. Bhowmick, R. Bise, H.J. Shin, G. Delgadino, B. Jariwala, D. Lambert, S. Deshmukh, "Highly selective etching of Silicon Dioxide Using Fluorocarbons"; AVS 61st International Symposium & Exhibition (2014);

9:40am **PS+SS+TF-FrM5 Chamber Wall Effect for Fluorocarbon Assisted Atomic Layer Etching of SiO_2 Using Cyclic Ar/C_4F_8 Plasma**, ***Masatoshi Kawakami***, Hitachi High-Technologies, Japan, *D. Metzler, C. Li, G.S. Oehrlein*, University of Maryland, College Park

The requirement for atomic scale etching is becoming more important with increasing miniaturization of semiconductor devices. A novel approach for oxide etching has been developed by Metzler et al [1]. Controlled etching of SiO_2 at the angstrom-level is based on steady-state Ar plasma and deposition of a thin reactive fluorocarbon layer enabled by precise, periodic C_4F_8 injection. High process stability is necessary for the success of this method and its use in mass production. Chamber wall interactions are crucial to the stability of this process. In this research, we studied the influence of chamber wall temperature and chamber wall chemical state on ALE process performance. The experiments were conducted in an inductively coupled plasma system excited at 13.56 MHz. The temperature of the quartz coupling window was measured with an infrared temperature sensor. *In situ* real time ellipsometry allows for film thickness measurements during the process. Plasma gas-phase chemistry was characterized by optical emission spectroscopy. We conducted the cyclic Ar/C_4F_8 SiO_2 ALE process using different initial chamber temperature, and chamber wall polymer coverage condition. It was found that although the polymer film thickness deposited in each cycle is constant, the etching behavior changed, likely related to a change in depositing species. Chamber wall temperature shows a clear effect on the CO and SiF emission and their relative ratio. When the surface of the quartz coupling window started to be covered by a fluorocarbon film, the overall CO and SiF intensity decreased while the CO/SiF emission peak ratio did not change. The relationship to observed etching behavior will be discussed.

The authors gratefully acknowledge financial support of this work from National Science Foundation (CBET-1134273) and US Department of Energy (DE-SC0001939).

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[1]D. Metzler, R. Bruce, S. Engelmann, E.A. Joseph, and G.S. Oehrlein, J Vac Sci Technol A **32**, 020603 (2014)

10:00am **PS+SS+TF-FrM6 Potential Solutions for Atomic Precision Etching**, ***Olivier Joubert***, LTM-CNRS, France, *E. Despiau-Pujo,* LTM, France, *G. Cunge,* LTM - CEA/LETI, France, *L. Vallier, J. Dubois, A. Tavernier,* Univ. Grenoble Alpes-CNRS-CEA/Minatec-LTM, France, *O. Luere, S. Banna, Y. Zhang*, Applied Materials **INVITED**

The continuous downscaling of device dimensions and introduction of new transistor architectures such as FDSOI or FINFEts transistors is bringing up new challenges for plasma etching technologies. For the gate transistor for example, future technological nodes require patterning capabilities in a range of dimension going below 10 nm. Extremely thin layers (less than 1nm) of materials are now involved in the stacks of materials to pattern requiring in some cases an etch precision better than 1 nm. In other words, the etch selectivity and physical/ chemical damage induced by the plasma must be controlled in a way such as the plasma can stop in a layer of materials as thin as 1nm without damaging the underlayers or the substrate material. Such a precision in processes becomes difficult to reach with the state of the art plasma technologies.

In this presentation, we will describe two plasma technologies that could potentially reach that goal.

A new Technology is the so-called "Thin Layer Etching" technology. In the first step of the TLE technology, H2 or He Ions produced by a capacitive plasma induce modification of silicon based materials while in a second step the modified material is removed in an all dry NF3/NH3 remote plasma that form volatile products with the modified silicon based materials. Performance achieved by TLE for nitride spacer etching will be shown and compared to conventional ICP results.

Fast gas pulsing technology could also be a promising way to form ultra-thin reactive layer during plasma processing, allowing atomic precision etching to be achieved. This concept will be explained and discussed based on preliminary result of silicon etching in chlorine plasmas using atomistic simulation.

10:40am **PS+SS+TF-FrM8 Molecular Dynamics Simulations of Atomic Layer Etching by Low Energy Ions**, ***Jun-Chieh Wang***, *S. Rauf, J.A. Kenney, L. Dorf, K.S. Collins*, Applied Materials Inc.

In the semiconductor industry, the use of atomic layer etching (ALE) makes it feasible to accurately control the critical dimensions to nanometer level or smaller. In ALE, the target substrate is first exposed to a reactive gas that passivates the surface, which is then followed by ion bombardment with energy below the sputtering threshold. It is critical to precisely control the ion energy and flux during the etching process to remove the topmost layer of the passivated surface without damaging the underlying substrate. Once the passivation layer is removed, the etch process stops. The passivation and etching steps are repeated until one has etched to the desired thickness. In contrast to conventional plasma etch processes, microfabrication using ALE promises high selectivity and low damage to the substrate.

In this presentation, we discuss the properties of ALE using results from molecular dynamics (MD) simulations. The simulation procedure is conceptually similar to those described in previous publications [1,2]. In this study, a crystalline Si(100)-(2x1) or amorphous surface (made by low energy Ar$^+$ ion bombardment) was generated and equilibrated at room temperature. The bottom layers were fixed in space, and the periodic boundary conditions were applied laterally to remove the boundary effect. The ions are modeled as energetic neutrals. The surface was passivated by repeated bombardment with low energy Cl atoms at normal incident, which was followed by Ar$^+$ or Cl$^+$ ion bombardment to remove the passivation topmost layers. The Berendsen scheme is used between ion/neutral impacts to remove the energy from the surface region and cool the surface layer to room temperature. The Stillinger Weber (SW) type potentials are used for Si-Si, Si-Cl and Cl-Cl interactions. The Ar-Si and Ar-Cl interactions were modeled using Moliere potentials. The leap-frog form of Verlet algorithm was used to numerically integrate the Newton's equation of motion. The MD is applied to study several variants of the ALE process. The fundamental properties of Si etching are also investigated for both bare and Cl-passivated Si surfaces with several ions including Ar$^+$, Cl$^+$ and Cl$_2^+$. These fundamental studies are used to interpret our layer-by-layer ALE experiments in our laboratory.

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11:00am **PS+SS+TF-FrM9 Atomic Layer Etching of InGaAs using Cl$_2$/Ar Ion Beam**, ***Jinwoo Park***, *D.H. Yun, H.S. Kim, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

Atomic layer etching can be one of next-generation etching techniques that can be applied to various materials including III-V compounds semiconducting materials such as indium-gallium arsenide (InGaAs) which is a great potential material due to the high carrier mobility for nano-scale devices. In this study, the atomic layer etching characteristics of InGaAs has been investigated using chlorine as adsorption gas and low energy Ar ion for desorption during the etch cycle to control the etch depth precisely and to minimize the surface damage of the material. For the chlorine adsorption, chlorine radical was adsorbed on the InGaAs surface and, during the desorption, the chlorine adsorbed InGaAs was removed by the Ar ion with the energy of about 20eV. By using the atomic layer etching technique, the controlled InGaAs etch depth per cycle and very high etch selectivity of InGaAs over dielectric materials such as silicon dioxide and hafnium dioxide could be obtained. The surface roughness of etched InGaAs characterized by atomic force microscopy was similar to that of un-etched InGaAs at the atomic layer etching condition.

11:20am **PS+SS+TF-FrM10 InGaN Quantum Nanodisks Fabrication by Bio-Template and Neutral Beam Etching**, ***Yi-Chun Lai***, National Chiao Tung University, Taiwan, Republic of China, *A. Higo, C. Thomas, C.Y. Lee, T. Tanikawa, K. Shojiki, S. Kuboya, R. Katayama,* Tohoku University, Japan, *T. Kiba,* Hokkaido University, Japan, *I. Yamashita,* Nara Institute of Science and Technology, Japan, *A. Murayama,* Hokkaido University, Japan, *P.Yu. Yu,* National Chiao Tung University, Taiwan, Republic of China, *S. Samukawa*, Tohoku University

III-N quantum dots (QDs) gain media have generated great interest because of their desirable properties such as low threshold and temperature independence due to the discrete nature of the density of states. A uniform and high-density two-dimensional (2D) array of an isolated QD structure is required when considering applications in visible wavelength such as white LED. In general, size distribution, uniformity, and high-density are trade-offs when using a conventional self-assembly method; therefore, we have developed a technique that integrates a bio-template with neutral beam etching (NBE) process.

In this work, quantum nanodisks (QNDs) were fabricated from InGaN/GaN single quantum well (SQW) by using a bio-template and NBE. We developed a damage-less, top-down fabrication process for achieving high density of QNDs such as 2 x 10^{11} cm^{-2} embedded in 10 nm in diameter and 20 nm high nanopillars. The fabricated QNDs have great potential for fabricating quantum optoelectronic devices because of controllable diameter and thickness.

The InGaN/GaN SQW wafer was grown on a 2-inch c-plane sapphire substrate by metal-organic vapor phase epitaxy (MOVPE). The structure consisted of a 1µm-thick GaN buffer layer, 3nm-thick In$_{0.1}$GaN and a 10nm-thick GaN capping layer. We used ferritins modified with polyethylene glycol (PEG ferritins) that include a metal oxide core for the etching mask. Oxygen annealing in vacuum was used to remove the ferritin protein shell at 350˚C, at chamber pressure of 32 Pa. Therefore the 7 nm diameter iron core was remained on the surface. Then hydrogen radial treatment, hydrogen passivation and NBE etching process were performed. At first, hydrogen radical treatment was realized to remove the surface oxide at chamber pressure of 32 Pa at 350˚C. Subsequently, hydrogen passivation was done to avoid any re-oxidation during the process. Finally, SQW was etched completely to form nanopillars using 40 sccm Cl$_2$ at a chamber pressure of 0.1 Pa, with a substrate temperature of 100˚C, ICP power of 800 W and bottom electrode bias power of 10W. As a result, InGaN/GaN 10 nm in diameter and 20 nm high nanopillars could be fabricated. The etching profile was confirmed by Transmission electron microscopy (TEM).

After etching, we measured the photoluminescence (PL) and time-resolved PL (TRPL) to observe the quantum confinement energy levels. According to the PL measurements, we found an energy shift of 1.25 eV, from 2.9eV for SQWs to 2.75eV for QNDs. Although these measurements are still on-going now, we will clearly analyze and discuss the phenomena related to this shift in energy in the near future.

11:40am **PS+SS+TF-FrM11 Towards a Nanoscale Plasma Etching Precision: Molecular Dynamics Simulations of Si-Cl Interactions**, ***Paulin Brichon***, Univ. Grenoble Alpes-CNRS-CEA/Minatec-LTM,38000 Grenoble-France*,* *E. Despiau-Pujo,* LTM, France*,* *O. Mourey,* Univ. Grenoble Alpes-CNRS-CEA/Minatec-LTM,38000 Grenoble-France*,* *G. Cunge,* LTM - CEA/LETI, France*,* *O. Joubert*, Univ. Grenoble Alpes-CNRS-CEA, France

Due to high ion bombardment energies and significant fragmentation rates, conventional CW plasma processes are not able to selectively etch ultrathin films without damaging the active layers of advanced nanoelectronic devices (FDSOI, FinFET). In order to achieve uniform and damage-free etching of sub-nm-thick materials, one alternative is to lower the electron temperature (T_e) of the plasma. This can be achieved temporally by pulsing the plasma (i.e. switching on and off the RF source power), which introduces two additional parameters to tune an etching process, the pulsation frequency and the duty cycle (DC). Pulsed-plasma discharges exhibit lower average ion energies (E_i~5-10eV); their chemical reactivity (or dissociation rate) can also be controlled by varying the DC. Another alternative is to lower T_e spatially, by segregating the electron heating region far from the wafer. These low-T_e plasmas are characterized by very low E_i (E_i<5eV) and high radical densities.

With lower E_i and controllable reactivity, these plasmas are promising to etch sub-nm-thick stacked materials. However, the interactions between reactive plasmas and surfaces are so complex that the efficient development of new processes can require numerical simulations. Therefore, we develop Molecular Dynamics (MD) simulations to understand the impact of various plasma technologies on the interactions between ultrathin Si films and Cl_2 plasmas under a wide range of plasma conditions. They help to understand the precise role of E_i in plasma-surface interactions, the relationship between the flux/energy of reactive species bombarding the surface and its structural/chemical modifications.

In this study, MD simulations - coupled with experiments - are performed to quantify modifications (plasma-induced damage, etch rate) of Si films after exposition to various Cl_2 plasma conditions, simulated by bombarding the substrate with both ion and neutral species. All simulations show the formation of a stable $SiCl_x$ reactive layer and a constant etch yield (EY) at steady state. The key plasma parameter to control the etching of ultrathin Si layers is E_i, which lowers both the damaged layer thickness and EY when it is decreased. The neutral-to-ion flux ratio (Γ) is the 2nd key parameter: its increase reduces the damaged layer thickness while the etch rate grows. While maintaining Γ constant, the neutral dissociation rate and the ion composition do not influence significantly the etching process. Etching simulations of a simple Si pattern are then compared to the etching of blanket silicon, focusing on phenomena such as ion channeling, passivation/damage of pattern sidewalls and top pattern erosion.

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 *RE*MnO$_3$ (*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.

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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^{o} and 30^{o} 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.

Thin Film
Room: 111 - Session TF+MI-FrM

Thin Films for Light Trapping, Plasmonic, and Magnetic Applications
Moderator: Angel Yanguas

8:20am **TF+MI-FrM1 Designing and Deposition of Multilayer Selective Surface for Tuning Absorption and Reflection of Solar Spectra**, *Z. Ren,* ***Feng Cao***, University of Houston **INVITED**

Spectrally-selective solar absorbers are widely used in solar hot water and concentrating solar power (CSP) systems. However, the performance at high temperatures (>500 ºC) can be further improved. Recent progress on cermet-based solar absorbers has shown promising high temperature thermal stability and wavelength selectivity. Here we explore W-Ni-Al_2O_3, W-Ni-YSZ (yttria-stabilized-zirconia), and W-Ni-SiO_2 cermet based spectrally selective surfaces for high-temperature solar absorber applications. The developed multilayer selective surfaces are deposited by magnetron sputtering on different substrates depending on applications. The absorber consists of two solar absorbing cermet layers with different W-Ni volume fraction inside the dielectric matrix, one or two anti-reflection coatings (ARCs), and one tungsten IR reflection layer for reduced IR emittance and improved thermal stability. All these absorbers show an absortance of > 90% for temperature up to 500 °C and emittance of ~5% at about room temperature and 10-15% at 500 °C.

Recently we are developing a new kind of absorber that reflects a certain range of wavelength and absorbs the rest of the whole solar spectra. The absorbed part is used for electrical power generation by steam engine and the reflected part is used for solar photovoltaic conversion. The thermal energy can be easily stored for later conversion to provide electrical power around the clock without worrying the Sun's night time.

9:00am **TF+MI-FrM3 Femtomagnetism in FePt Nanoparticles for Heat Assisted Magnetic Recording**

J-Y. Bigot, J. Kim, M. Vomir, Institut de Physique et Chimie des Matériaux de Strasbourg: Université de Strasbourg and CNRS, France*, O. Mosendz, S. Jain,* ***Dieter Weller***, HGST a Western Digital company **INVITED**

Implementing larger and faster recording capacities, like in Heat Assisted Magnetic Recording (HAMR) devices, requires investigating the magnetization dynamics of nanostructures at the sub-picosecond time scale. The case of $L1_0$ FePt "nanocrystals" is of particular interest as HAMR media can be designed with grain diameter below today's D ~ 8 nm. The magnetic anisotropy is sufficiently high and results in coercive fields larger than 5 Tesla at room temperature [1, 2].

Femtosecond magneto-optics allows investigating the dynamical properties of such films [3] and nanoparticles [4] with a temporal resolution well adapted to the actual needs of performant materials that can be addressed in the time scale of a few picoseconds or faster. In the case of materials for HAMR, the pre-heating with femtosecond laser pulses allows reaching very high electron temperatures beyond the Curie point without over heating the lattice. It is therefore a relevant approach to use femtosecond pulses as it allows improving the conditions for obtaining an efficient switching due to the laser pre-heating. In that context, the variation of the coercive field H_c and magnetization at saturation M_S are important quantities to be characterized. We have investigated such dynamics in $L1_0$ FePt nanoparticles and accurately characterized the nonlinear variation of M_S and H_c upon varying the laser density of energy. We demonstrate that the Curie temperature can be reached during a few hundreds of femtoseconds, showing that the speed for addressing bits of information can be further improved in ultrafast HAMR applications.

[1] O. Mosendz, et al., J. Appl. Phys. 111, 07B729 (2012)

[2] D. Weller et al., Phys. Stat. Solidi A 210, 1245 (2013)

[3] S. Wicht et al., J. Appl. Phys. 114, 063906 (2013) & J. Appl. Phys. 117, 013907 (2015)

[4] E. Beaurepaire, J.-C. Merle, A. Daunois, J.-Y. Bigot, Phys. Rev. Lett. 76, 4250 (1996)

[5] J.-Y. Bigot, M. Vomir, Annalen der Physik 525, 2–30 (2013)

10:00am **TF+MI-FrM6 Application of High Refractive Index Layers to Perfect Absorbers for Solar and Thermal Radiations**

Motofumi Suzuki*, K. Nishiura, S. Masunaka, K. Namura*, Kyoto University, Japan

In this presentation, we demonstrate that high refractive index materials such as β-$FeSi_2$ are key to achieve anti-reflective interference coatings on an opaque substrate. B-$FeSi_2$ is known as an eco-friendly semiconductor and its bulk refractive (*n*) and extinction (*k*) indices are higher than 5 and zero, respectively, in infrared (IR) region ($\lambda > 1.55$ μm). We have reported that the high refractive index of β-$FeSi_2$ is quite useful to reduce the reflectance of metal substrates and that β-$FeSi_2$ thin films/stainless steel substrate systems show nice spectrally selective absorption properties in IR region. For sputtered polycrystalline β-$FeSi_2$ thin films, we recently found that $k \approx 0.3$ in IR region, which is different from the bulk value. Thus, we redesigned antireflective-layered structures on an opaque substrate and prepared them. As the results, a system of β-$FeSi_2$/W shows perfect absorption properties, where absorptance reaches higher than 99% at desired wavelength regions, while that in other regions is lower than a few %. On the other hand, another interesting optical property of β-$FeSi_2$ is that both *n* and *k* are considerably high in visible to NIR region ($\lambda < 1.55$ μm). This enables us to design multilayered broadband absorbers for VIS to $\lambda < 2.0$ μm. The designed multilayers consist of SiO_2/β-$FeSi_2$/SiO_2/β-$FeSi_2$/W, where the upper β-$FeSi_2$ layer absorbs VIS and NIR ($\lambda < 1.0$ μm) and the bottom β-$FeSi_2$ layer/W absorbs IR (1.0 μm<λ<2.0 μm). The optimized multilayers absorb more than 95% of solar energy and the eminence at 450 °C is lower than 6%. No significant change in absorptive properties in both single and multilayered absorbers has been recognized after they are annealed in air at least up to 500 °C. The perfect absorbers with high refractive index layers are useful for applications to solar selective absorbers for solar thermal power generation and spectrally selective thermal emitters for thermophotovoltaic power generation, IR heaters, radiation cooling.

10:20am **TF+MI-FrM7 Antireflection Coatings for Tandem Solar Cells**

Bo Yuan, University of Delaware*, B. Thibeault,* University of California at Santa Barbara*, K. Dobson,* University of Delaware*, A. Barnett,* University of New South Wales, Australia*, R.L. Opila*, University of Delaware

Because of the ability to exploit multiple absorption bands, Multi-junction Solar Cells (MJSCs) are the most efficient solar cells ever developed. As on single junction solar cells, Antireflection Coatings (ARCs) are utilized to achieve broadband absorption. Due to the fact that the total current of MJSCs is limited by the subcell that has the lowest generated current, ARCs on MJSCs must have the ability to minimize light loss at the range of limiting cell, but optimally all across the visible spectrum.

Unlike conventional Double Layer Antireflection Coatings (DLARCs) that can only reduce light reflection at certain wavelengths, moth eye structures are able to mitigate light loss over broadband wavelength due to their smooth change of refractive index. We report the fabrication of such a Subwavelength Structure (SWS) by using wet etching and dry etching of dielectric materials. Silicon wafers are used here as the substrate to test the quality of ARCs. ZnO has been chosen as one dielectric material because of its excellent transmittance and durability. It also has a close index match to the underlying GaInP window layer in this tandem cell. Wet etching using oxalic acid has been utilized here to texture the ZnO surface because it is a simple and cost-effective method. A low reflection (less than10%) over a broad range of wavelength (400-970nm) has been achieved. However, it turns out that wet etching is not very controllable and cannot fabricate the high aspect ratio periodic structure necessary for optimal absorption. A $Zn(C_2O_4)$ $2H_2O$ bulk phase was found on the ZnO surface.

Thus, lithography and plasma etching have been employed because of their better process control capability and less dependence on the crystalline orientation of the material. We then switched to using Ta_2O_5 since it has similar optical properties to ZnO and also a broad bandgap to ensure its transparency. Dry etching of Ta_2O_5 gives us nanocones with aspect ratio (height over base diameter) of 1.26. At an angle of 8 degree from normal incidence, textured Ta_2O_5 achieved the averaged reflection as low as 6% over 320-900nm and itoutperforms DLARCs and textured ZnO over a wide range of wavelength. Future work will focus on fabricating this moth eye structure on III-V/SiGe tandem cells and simulating the reflectance spectra using Finite Difference Time Domain methods.

10:40am **TF+MI-FrM8 Preparation and X-ray Characterization of Highly Oriented Magnetic and Magnetoelectric Thin Films**

Radomir Kuzel, Charles University in Prague, Czech Republic*, J. Bursik, M. Soroka, K. Knizek*, Academy of Sciences of the Czech Republic

Different kind of thin films with remarkable magnetic and magnetoeletric properties require strong preferred orientation in order to utilize strong anisotropy of their properties.

The main aim of the work is to prepare the films of hexagonal ferrites showing magnetoelectric effects. There are several types of these materials marked as e.g. M-type [$(Ba,Sr)Fe_{12}O_{19}$, space group $P6_3/mmc$], Y-type [$(Ba,Sr)_2Me_2Fe_{12}O_{22}$, s. g. R-3m], Z-type [$(Ba,Sr)_3Me_2Fe_{24}O_{41}$, s. g. $P6_3/mmc$], and others. Our attention was focussed mainly to Y-type where the best properties are expected. All these lattices are long along *c*-axis and this should be oriented perpendicular to the surface. The films were prepared through the chemical solution method either on $SrTiO_3$ (111) or sapphire Al_2O_3 (0001) substrates, respectively. We are looking not only for suitable substrates but also we have succeeded in using seed template interlayers, for example M hexaferrite $SrFe_{12}O_{19}$. A detailed inspection revealed that growth of seed layers starts through the break-up of initially continuous film into isolated grains with expressive shape anisotropy and hexagonal habit. Promising type of such seed layers seem also to be $SrAl_{12}O_{19}$ films where two kinds of preparation were investigated – deposition of $SrAl_{12}O_{19}$ onto sapphire substrate and reaction SrO + Al_2O_3.

Other type of magnetic films studied were magnetic spinels Co_3O_4 prepared by decomposition of films of layered cobaltates Na_xCoO_2 deposited by chemical solution deposition method and grown on sapphire substrates.

The films were characterized mainly by AFM and by several XRD techniques. Phase transitions and thermal stability were studied in symmetric Bragg-Brentano geometry, degree of preferred orientation by rocking curves (omega scans) and phi scans of asymmetric reflections, pole figures and also by reciprocal space maps. Residual stresses were also tested but they were usually zero or negligible. All the films were strongly oriented with the planes parallel to the surface but different kind of in-plane orientations was observed often structures with with several domains.

11:00am **TF+MI-FrM9 Size Effects on the Order-Disorder Phase Transition Temperature in FeNiPt Nanoparticles**

G. Sutherland, D. Wood, Brigham Young University*, A. Warren, K. Coffey,* University of Central Florida*,* ***Richard Vanfleet***, Brigham Young University

Chemically ordering metal alloys such as FePt are hard magnets and good candidates for magnetic data storage in their ordered phase but not in the disordered state. The order-disorder phase transition temperature is impacted by the size of the particle with surface energies becoming significant for nanometer sized particles. Theoretical and computational approaches have predicted lowering of phase transition temperatures as the particle size decreases. Experimental evidence is more limited. Observation of ordering in nanoparticles is a complex interplay between thermodynamic and kinetic factors. Using Fe-Ni pseudo binary alloys with Pt allows isolation of thermodynamic variables. We see a size dependent reduction of order-disorder temperature in this system with particles in the 5 – 12 nm range. At 6 nm the reduction is ~15%

11:20am **TF+MI-FrM10 A Comparison of Heptane Solvent Annealing versus Thermal Annealing Block Copolymers for Bit Patterned Advanced Media**, ***Allen Owen***, *A. Montgomery, H. Su, S. Gupta*, University of Alabama

Hard disk drive storage media is trending towards both smaller physical size and greater storage capacity by increasing the areal density of the magnetic storage media. Bit patterning shows potential as a method for increasing this areal density. A block copolymer template can be used to provide an etch mask for bit patterning a magnetic thin film. Statistical designs of experiments were carried out comparing the effect of nanopatterning via ion milling Co/Pd multilayers using two different annealing methods for PS-PFS block copolymers. The design of experiments for each annealing method varied the etch angle, etch time and etch power during ion milling. Wafers that were sputter-deposited with Co/Pd multilayered thin films were spin-coated with PFS block copolymer and solvent annealed under heptane vapor in an oil bath at 35 °C for 6 hours. Identical wafers were thermally annealed in atmosphere at 140 °C for 48 hours. After annealing, the films were ashed in oxygen to remove the PS, leaving the PFS spheres as masks for the subsequent ion milling. The results from each annealing study showed that nanopillars with a nominal size of ~ 30 nm have been fabricated. The thermally annealed Co/Pd multilayers yielded a 407% increase in coercivity to ~6.6 kOe, while the heptane annealed thin film resulted in a 223% increase to ~4.2 kOe. A statistical design of experiments comparing two different etch techniques:(i) inductively coupled plasma reactive ion etching (ICP-RIE) and (ii) ion milling was carried out for these two annealing methods. The results indicate that process optimization can be achieved with a combination of the correct annealing and etching techniques.

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:

[1] Jacobs, T.D.B. and Carpick, R.W. "Nanoscale Wear as a Stress-Assisted Chemical Reaction," Nature Nanotech., 8, 2013, 108-112.

[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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