2D Materials Focus Topic
Room: 310 - Session 2D+EM+NS+PS+SS+TF-MoM

2D Materials Growth and Processing
Moderator: Thomas Greber, University of Zurich

8:20am **2D+EM+NS+PS+SS+TF-MoM1 Exploring the Flatlands: Synthesis, Characterization and Engineering of Two-Dimensional Materials**, ***Jun Lou***, Rice University **INVITED**

In this talk, we report the controlled vapor phase synthesis of MoS_2 atomic layers and elucidate a fundamental mechanism for the nucleation, growth, and grain boundary formation in its crystalline monolayers. The atomic structure and morphology of the grains and their boundaries in the polycrystalline molybdenum disulfide atomic layers are examined and first-principles calculations are applied to investigate their energy landscape. The electrical properties of the atomic layers are examined and the role of grain boundaries is evaluated. More importantly, if precise two-dimensional domains of graphene, h-BN and MoS_2 atomic layers can be seamlessly stitched together, in-plane heterostructures with interesting electronic applications could potentially be created. Here, we show that planar graphene/h-BN heterostructures can be formed by growing graphene in lithographically-patterned h-BN atomic layers. Our approach can create periodic arrangements of domains with size that ranging from tens of nanometers to millimeters. The resulting graphene/h-BN atomic layers can be peeled off from their growth substrate and transferred to various platforms including flexible substrate. Finally, we demonstrate how self-assembled monolayers with a variety of end termination chemistries can be utilized to tailor the physical properties of single-crystalline MoS_2 atomic-layers. Our data suggests that combined interface-related effects of charge transfer, built-in molecular polarities, varied densities of defects, and remote interfacial phonons strongly modify the electrical and optical properties of MoS_2, illustrating an engineering approach for local and universal property modulations in two-dimensional atomic-layers.

9:00am **2D+EM+NS+PS+SS+TF-MoM3 Influence of Substrate Orientation on the Growth of Graphene on Cu Single Crystals**, ***Tyler Mowll***, University at Albany-SUNY, *Z.R. Robinson,* U.S. Naval Research Laboratory, *P. Tyagi, E.W. Ong, C.A. Ventrice, Jr.*, University at Albany-SUNY

A systematic study of graphene growth on on-axis Cu(100) and Cu(111) single crystals oriented within 0.1° from the surface normal and a vicinal Cu(111) crystal oriented 5° off-axis has been performed. Initial attempts to grow graphene by heating each crystal to 900°C in UHV, followed by backfilling the chamber with C_2H_4 at pressures up to $5x10^{-3}$ Torr did not result in graphene formation on either the on-axis Cu(100) or on-axis Cu(111) surfaces. For the vicinal Cu(111) surface, epitaxial graphene was formed under the same growth conditions. By backfilling the chamber with C_2H_4 before heating to the growth temperature, epitaxial graphene was formed on both the on-axis Cu(100) and off-axis Cu(111) surfaces, but not the on-axis Cu(111) surface. By using an argon overpressure, epitaxial overlayers could be achieved on all three Cu substrates. These results indicate that the most catalytically active sites for the dissociation of ethylene are the step edges, followed by the Cu(100) terraces sites and the Cu(111) terrace sites. The need for an argon overpressure to form graphene the on-axis Cu(111) surface indicates that the Cu sublimation rate is higher than the graphene growth rate for this surface. This research was supported in part by the NSF (DMR-1006411).

9:20am **2D+EM+NS+PS+SS+TF-MoM4 Synthesis of Large Scale MoS_2-Graphene Heterostructures**, ***Kathleen McCreary****, A.T. Hanbicki, J. Robinson, B.T. Jonker*, Naval Research Laboratory

A rapidly progressing field involves the stacking of multiple two-dimensional materials to form heterostructures. These heterosctructures have exhibited unique and interesting properties. For the most part, heterostructure devices are produced via mechanical exfoliation requiring the careful aligning and stacking of the individual 2D layered components. This tedious and time consuming process typically limits lateral dimensions to micron-scale devices. Chemical vapor deposition (CVD) has proven to be a useful tool in the production of graphene and has very recently been investigated as a means for the growth of other 2D materials such as MoS_2, $MoSe_2$, WS_2, WSe_2 and hexagonal boron nitride. Using a two-step CVD process we are able to synthesize MoS_2 on CVD grown graphene. AFM, Raman spectroscopy, and Photoluminescence spectroscopy of the MoS_2-graphene heterostructure show a uniform and continuous film on the cm scale.

9:40am **2D+EM+NS+PS+SS+TF-MoM5 Growth of 2D MoS_2 Films by Magnetron Sputtering**, ***Andrey Voevodin***, Air Force Research Laboratory, *C. Muratore,* University of Dayton, *J.J. Hu,* Air Force Research Laboratory/UDRI, *B. Wang, M.A. Haque,* Pennsylvania State University, *J.E. Bultman, M.L. Jesperson,* Air Force Research Laboratory/UDRI, *P.J. Shamberger,* Texas A&M University, *R. Stevenson,* Air Force Research Laboratory, *A. Waite,* Air Force Research Laboratory/UTC, *M.E. McConney, R. Smith*, Air Force Research Laboratory

Growth of two dimensional (2D) MoS2 and similar materials over large areas is a critical pre-requisite for seamless integration of next-generation van der Waals heterostructures into novel devices. Typical preparation approaches with chemical or mechanical exfoliation lack scalability and uniformity over appreciable areas (>1 mm) and chemical vapor deposition processes require high substrate temperatures. We developed few-layer MoS_2 growth under non-equilibrium magnetron sputtering conditions selected to minimize the MoS_2 nucleation density and maximize 2D growth of individual crystals [1]. In this process, the thermodynamically driven tendency to form islands is accomplished by maximizing atomic mobility through the control of incident flux kinetic energies, densities, and arriving angle to the substrate while avoiding defect formation (i.e., vacancy creation by sputtering of S atoms). Amorphous SiO_2, crystalline (0001) oriented Al_2O_3, and (002) oriented graphite substrates were used to grow few monolayer thick MoS_2 films. Continuous 2D MoS_2 films were produced over 4 cm^2 areas. They were composed of nano-scale domains with strong chemical binding between domain boundaries, allowing lift-off from the substrate and electronic transport measurements with contact separation on the order of centimeters. Their characteristics were similar to few-layer MoS_2 films produced by exfoliation with a direct band gap in thin samples of approximately 1.9 eV from photoluminescense spectra. The electron mobility measured for as-grown MoS_2 films was very strongly dependent on film thickness and substrate choice.

[1] "Continuous ultra-thin MoS2 films grown by low-temperature physical vapor deposition", C. Muratore, J.J. Hu, B. Wang, M.A. Haque, J.E. Bultman, M. L. Jesperson, P.J. Shamberger, A.A. Voevodin, Applied Physics Letters (2014) in press.

10:00am **2D+EM+NS+PS+SS+TF-MoM6 Formation of Graphene on the C-face of SiC{0001}: Experiment and Theory**, ***Jun Li****, G. He, M. Widom, R.M. Feenstra*, Carnegie Mellon University

There are two {0001} surfaces of SiC, the (0001) surface known as the "Si-face", and the (000-1) surface or "C-face". The formation of graphene (by heating the SiC to 1100 – 1600 ° C in various gaseous environments) has been studied for both surfaces, although it is much better understood on the Si-face. In that case, an intermediate C-rich layer, or "buffer layer" forms between the graphene and the SiC crystal. This buffer layer has $6\sqrt{3}x6\sqrt{3}$-R30° symmetry; its structure is well established,[1] and it acts as a template for the formation of subsequent graphene layers. In contrast, graphene formation on the C-face is much less well understood. More than one interface structure between the graphene and the SiC has been observed,[2,3] and, with one notable exception,[4] the quality of the graphene formed on the C-face is generally lower than that for the Si-face.

In this work we provide new experimental and theoretical results that allow us to understand graphene formation on the C-face of SiC. Experimentally, by heating the SiC in a disilane environment, we map out the phase diagram of different surface and interface structures that form on the SiC as a function of disilane pressure and sample temperature. New surface structures that develop just prior to the graphene formation are observed. With additional heating, graphene forms on the surface, but some remnant of the surface structure prior to the graphene formation is believed to persist at the graphene/SiC interface. From first-principles theory, we find that the hydrogen in the disilane environment plays a critical role in the surface/interface structures that form. Experimentally, for disilane pressures below $5x10^{-5}$ Torr, we find a 2x2 surface structure forming prior to graphene formation. From theory we identify this structure as consisting of a silicon adatom together with a carbon restatom on the surface, with H-termination of those atoms being possible but not necessary. At higher disilane pressures we observe a 4x4 structure, and we identify that as consisting of a lower density of Si adatoms than the 2x2, now with at least some of the adatoms and restatoms being H-terminated. With graphene formation, this structure converts to the observed $\sqrt{43}x\sqrt{43}$-R± 7.6° interface structure. At higher disilane pressures we theoretically predict the formation of a surface consisting simply of H-terminated carbon restatoms. Experiments are underway to observe that surface, along with subsequent graphene formation on the surface.

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(4) W. A. de Heer et al., PNAS **108**, 16900 (2011).

10:40am **2D+EM+NS+PS+SS+TF-MoM8 Graphene on Hexagonal Boron Nitride Heterostacks Grown by UHV-CVD on Metal Surfaces**, ***Juerg Osterwalder***, *S. Roth, A. Hemmi,* University of Zurich, Switzerland, *F. Matsui,* Nara Institute of Science and Technology, Japan, *T. Greber*, University of Zurich, Switzerland **INVITED**

Chemical vapor deposition (CVD) performed under ultra-high vacuum conditions on single-crystal metal surfaces enables the growth of large-area and high-quality graphene and hexagonal boron nitride (h-BN) single layers. We explore the CVD parameter space of precursor pressure and temperature in order to go beyond the self-saturating single-layer growth, or to grow heterostacks of the two materials. Formed layers are characterized structurally by LEED, STM and x-ray photoelectron diffraction. On Cu(111) a graphene layer could be grown on a pre-deposited single layer of h-BN when using 3-pentanone as a precursor at a pressure of 2.2 mbar and a substrate temperature of 1100 K [1]. On Rh(111) the same procedure leads to incorporation of carbon into the metal surface layers, while a graphene layer is formed only upon a second high-pressure dose [2]. In both cases the heterostructures show clearly the stacking sequence and structural and ARPES signatures of graphene on h-BN but are far from defect-free.

[1] S. Roth et al., Nano Lett. 13, 2668 (2013).

[2] S. Roth, PhD Thesis, Department of Physics, University of Zurich (2013).

11:20am **2D+EM+NS+PS+SS+TF-MoM10 Kinetics of Monolayer Graphene Growth by Carbon Segregation on Pd(111)**, ***Abbas Ebnonnasir***, *H.S. Mok, Y. Murata,* University of California at Los Angeles, *S. Nie, K.F. McCarty,* Sandia National Laboratories, *C.V. Ciobanu,* Colorado School of Mines, *S. Kodambaka*, University of California at Los Angeles

In this research, using in situ low-energy electron microscopy and density functional theory calculations, we elucidate the growth kinetics of monolayer graphene on single-crystalline Pd(111). In our experiments, carbon saturated Pd(111) samples were cooled down from 900 °C to segregate carbon on the surface in the form of graphene. Upon cooling the substrate, graphene nucleation begins on bare Pd surface and continues to occur during graphene growth. Measurements of graphene growth rates and Pd surface work functions along with DFT calculations establish that this continued nucleation is due to increasing C adatom concentration on the Pd surface with time. We attribute this anomalous phenomenon to a large barrier for attachment of C adatoms to graphene coupled with a strong binding of the non-graphitic C to the Pd surface.

Actinides and Rare Earths Focus Topic
Room: 301 - Session AC+AS+MI+SA+SS-MoM

Spectroscopy, Microscopy and Dichroism of Actinides and Rare Earths
Moderator: David Shuh, Lawrence Berkeley National Laboratory

8:20am **AC+AS+MI+SA+SS-MoM1 Novel Synthetic and Spectroscopic Techniques in Actinide Materials Chemistry**, ***Stefan Minasian***, Lawrence Berkeley National Laboratory, *E. Batista,* Los Alamos National Laboratory, *C.H. Booth,* Lawrence Berkeley National Laboratory, *D. Clark,* Los Alamos National Laboratory, *J. Keith,* Colgate University, *W. Lukens,* Lawrence Berkeley National Laboratory, *S. Kozimor, R.L. Martin,* Los Alamos National Laboratory, *D. Nordlund,* SLAC National Accelerator Laboratory, *D. Shuh, T. Tyliszczak,* Lawrence Berkeley National Laboratory, *D. Sokaras,* SLAC National Accelerator Laboratory, *X.-D. Weng,* Los Alamos National Laboratory, *T.-C. Weng*, SLAC National Accelerator Laboratory **INVITED**

The development of a detailed, quantitative understanding of electronic structure and bonding for a broad range actinide materials remains a significant scientific challenge. Recent advances have shown that the 1s to np transition intensities measured by Cl and S K-edge X-ray absorption spectroscopy (XAS) directly relate to coefficients of covalent orbital mixing in M–Cl and M–S bonds. The scientific progress associated with these Cl and S XAS studies suggests that using synchrotron-generated radiation to quantify covalency for ligands beyond Cl and S would have a wide impact. The nature of chemical bonds between actinides and light atoms such as oxygen, nitrogen, and carbon is of particular interest because these interactions control the physics and chemistry of many technologically important processes in nuclear science. However, obtaining accurate light atom K-edge XAS spectra on non-conducting compounds is notoriously difficult, because the measurement is highly sensitive to surface contamination, self-absorption, and saturation effects. Fortunately, recent upgrades at synchrotron facilities, advancements in beamline instrumentation, and sample preparation methods suggest that these insights are now within reach. Specifically, comparing XAS spectra measured in transmission with a scanning transmission X-ray microscope (STXM) with those from non-resonant inelastic X-ray scattering (NIXS) and time-dependent density functional theory provides a sound basis for validation of bulk-like excitation spectra.

Herein, a new effort is discussed that employs these techniques to understand bonding interactions in two well defined series of f-element materials. The actinide sandwich complexes, “actinocenes,” $(C_8H_8)_2An$ (An = Th, Pa, U, Np, Pu) have played a central role in the development of organoactinide chemistry. Results showed two contrasting trends in actinide–carbon orbital mixing, and evidence that covalency does not increase uniformly as the actinide series is traversed. Additionally, the C K-edge XAS spectrum of thorocene represents the first experimental evidence of a ϕ-type orbital interaction. Oxygen K-edge XAS measurements and DFT studies began the lanthanide dioxides LnO_2 (Ln = Ce, Pr, Tb), because their electronic structures are well-established from hard X-ray spectroscopies. Preliminary efforts to use lanthanide oxides and lanthanide organometallics as experimental benchmarks for quantitative determinations of covalency in d-block and f-block materials will also be discussed.

9:00am **AC+AS+MI+SA+SS-MoM3 X-ray Magnetic Circular Dichroism of Actinides**, ***Andrei Rogalev***, *F. Wilhelm*, European Synchrotron Radiation Facility (ESRF), France **INVITED**

Actinides compounds, which are straddling the magnetic properties of rare-earths and transition metals, have been the subject of increasing interest due to their very different properties, such as Pauli paramagnets, localized and itinerant ferromagnets, and heavy fermion superconductors. The key parameter responsible for the large variety of magnetic properties is obviously degree of localization of the 5f states which are indeed involved in both the chemical bonding and the magnetism. To unravel the details of the electronic structure and magnetic properties of these 5f states, polarization dependent X-ray spectroscopy at the $M_{4,5}$ edges appears as the most suitable experimental tools. At the third generation synchrotron radiation facilities, small x-ray beam with flexible polarization sized down to few microns can be routinely achieved. This technique is thus perfectly suited for studying minute samples (a few micrograms) of transuranium materials. This talk reviews recent advances in use of polarized x-rays to study local magnetic properties and electronic structure of actinides compounds.

The magnetic properties are mostly studied with X-ray Magnetic Circular Dichroism (XMCD). The great advantage of this technique is its capability to probe the orbital and spin magnetization of 5f states separately. XMCD experiments have been reported for a great number of uranium compounds and have permitted to understand, at least qualitatively, which is the ground state despite the difficulty over assigning a valency. It has also revealed differences between localized and itinerant systems that are not yet fully understood. To our knowledge there are very few reports on XMCD measurements on other trans-uranium materials. This is unfortunate, as the questions of localization of 5*f* states become more interesting as the 5*f* count increases. In order to improve our understanding of the magnetism of actinides, which is based up to now solely on uranium compounds, and thus better to describe the differences between localized and itinerant 5*f* systems, we report a thorough XMCD study of a series of ferromagnetic $AnFe_2$ Laves-phase compounds. Moreover, we show that additional information regarding exchange interaction between neighboring actinides atoms can be extracted from the XMCD measurements performed at absorption edges of other "nonmagnetic" atoms in the compounds.

Finally, we demonstrate that the study of the branching ratio in $M_{4,5}$ absorption spectra can bring valuable information regarding the coupling scheme, within which to discuss the electronic and magnetic properties of actinides atoms.

9:40am **AC+AS+MI+SA+SS-MoM5 Magnetic Circular Dichroism Measured with Transmission Electron Microscope**, ***Jan Rusz***, Uppsala University, Sweden **INVITED**

X-ray magnetic circular dichroism (XMCD; [1]) is an established experimental probe of atom-specific magnetic properties of lanthanides and actinides. In XMCD, a photon of well-defined energy and polarization is absorbed by an atom in the sample with a probability that is proportional to the number available unoccupied states with an energy that allows fulfilling the energy conservation and selection rules. An essential element of XMCD are so called sum rules [2,3], which relate the XMCD spectra to the spin and orbital angular momenta, respectively.

Recently, a new experimental method has been developed that is closely related to XMCD. It was named electron magnetic circular (or chiral) dichroism (EMCD) and it is measured with a transmission electron microscope (TEM) instead of a synchrotron beam-line. We will review the short history of this method starting from its proposal in 2003 [4], first experimental proof-of-the-concept in 2006 [5], formulation of the theory [6] and sum rules [7,8] in 2007 to the present state-of-the-art and early applications, for example [9-12]. Yet, despite intense efforts, EMCD is still in its development phase, particularly from the point of view of quantitative studies. On the other hand, qualitative EMCD experiments have reached resolutions below 2nm [13].

The primary advantages of the EMCD, when compared to XMCD, are costs, availability and lateral resolution. Even a state-of-the-art TEM is a device considerably cheaper than a synchrotron beam-line and as such it can be available locally to a research group. TEM is also a very versatile instrument that combines diffraction experiments, elemental analysis, local electronic structure studies via electron energy loss spectroscopy [14] and now also magnetism via EMCD.

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10:40am AC+AS+MI+SA+SS-MoM8 The Microstructure of Plutonium Hydride Growth Sites

***Martin Brierley**, J.P. Knowles,* AWE, UK*, M. Preuss, A.H. Sherry*, University of Manchester, UK

Under certain conditions plutonium is able to form plutonium hydride during long term storage [1]. Plutonium is radioactive, decaying via release of an alpha particle. Alpha particles are particularly damaging within the body and every attempt should be made to limit the distribution of loose material. Plutonium hydrides have been shown to be pyrophoric when exposed to oxygen; a reaction that could potentially liberate loose particulate outside of suitable containment.

Previous work into the hydriding rate of plutonium has investigated the reaction rate of various hydrides on the surface of these materials; specifically the nucleation rate, the lateral growth rate and the specific hydriding rate [2, 3]. Plutonium is a reactive metal and quickly forms a semi-protective oxide layer in air. Upon exposure of an oxide-covered sample to hydrogen, hydride is formed at discrete sites on the surface, which then grow radially across the surface [1]. Recent work has suggested a grain boundary enhanced growth rate [4].

In the present study, the microstructure associated with selected plutonium hydride growth sites was studied to provide information regarding the nucleation and growth mechanisms that govern the formation of plutonium-hydride. The samples were ground to 600 grit and evacuated before being exposed to ultra-pure hydrogen at pressures between 10 mbar and 1000 mbar for sufficient time to have nucleated a number of hydride sites.

Post-test analysis was performed using Scanning Electron Microscopy (SEM) and Optical Microscopy (OM) to determine the microstructure of the hydride growth sites. The morphology of individual hydride growth sites indicates that the hydride-metal interface has a highly discontinuous boundary, resulting from enhanced grain boundary diffusion and spears of transformed material; the microstructure within the plutonium hydride growth sites indicates that a preferred growth habit was adopted by the hydride product.

References

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11:00am AC+AS+MI+SA+SS-MoM9 Hydrides of U-Mo and U-Zr Alloys: Structure and Electronic Properties

***Ladislav Havela**, M. Paukov, I. Tkach, D. Drozdenko, M. Cieslar, Z. Matej*, Charles University, Czech Republic

When U metal (α-U) is exposed to H gas, it forms a stable hydride β-UH_3. The lattice expansion stabilizes the ferromagnetic order with the Curie temperature around 170 K. The metastable form, α-UH_3, could not be synthesized as a pure phase, and the admixture of β-UH_3 did not allow to determine reliably its intrinsic magnetic properties. We have been testing the reaction to H exposure of γ-U (bcc), which was synthesized as a single phase by combination of Mo or Zr doping into U and ultrafast cooling. We found that such alloys need high H_2 pressure and long exposure to absorb hydrogen. The products can be characterized by the formula $UH_3Mo(Zr)_x$. The hydrides with Mo have a structure corresponding to β-UH_3 with grain size around 1 nm, i.e. almost amorphous. Its ordering temperatures increase to 200 K for $UH_3Mo_{0.18}$ and then decrease for higher Mo concentrations. The hydrides UH_3Zr_x exhibit the UH_3 structure (bcc U lattice filled with H atoms). Their Curie temperature weakly decreases with increasing Zr concentration and the extrapolation to Zr-free state indicates T_C = 170 K, i.e. identical to β-UH_3. The results can be compared with numerous hydrides obtained by hydrogenation of U_6X compounds (X = Mn, Fe, Co, Ni), all probably having similar magnetic properties. We present a detailed study of magnetic properties, electrical resistivity and specific heat. The structure characterization of initial alloys and the hydrides has been done by means of XRD, SEM with EBSD and TEM. The hydrides represent and new class of U materials, which exhibit, irrespective of details of composition or crystal structure, strong ferromagnetism with relatively very high ordering temperatures, quite surprising at materials at which the inter-U spacing does not exceed appreciably the Hill limit 340-360 pm. At last, the variations using double doping (both Mo and Zr) will be presented.

11:20am AC+AS+MI+SA+SS-MoM10 Unraveling the Mystery of Reactively-Sputtered UO(4+x)

***David Allred**, R.S. Turley, B.S. McKeon, A. Diwan, E.A. Scott, R.R. Vanfleet*, Brigham Young University

We recently found EDX and XPS evidence in reactive sputtered uranium oxide thin films of higher oxygen-to-uranium ratios than the 3-to-1 allowed by stoichiometry. We used reactive, DC-magnetron sputtering in 100% oxygen to prepare uranium-oxide thin films on silicon wafer with the highest possible oxygen content to investigate this. Both EDX & XPS showed that the ratio of oxygen-to-uranium in freshly samples was at least 4-to-1, with compositions approached 5 to 1. The potential explanations are uranates or peroxides. Detecting hydrogen- and an element difficult to detect in thin films-is crucial in understanding what is happening chemically. Uranates require cations. The only one possible in our films would be hydrogen. Similarly, bulk uranium peroxides without water/ hydrogen peroxide of hydration are not known. (We have found evidence of uranium trioxide being weekly hygroscopic and stored samples in a dry environment, nonetheless these samples show high oxygen contents as prepared.) We report our chemistry and structural (TEM and XRD) attempts to solve this mystery. We also report are measurement of extreme ultraviolet reflectance of this material. (ALS-beamline 6.3.2)

11:40am AC+AS+MI+SA+SS-MoM11 Cathodoluminescence and Band Gap Studies of Single Crystal $U_xTh_{1-x}O_2$ (x = 0.00, 0.01, 0.22)

***David Turner**,* Oak Ridge Institute for Science and Education*, J. Reding, R. Hengehold, T. Kelly,* Air Force Institute of Technology*, J.M. Mann,* Air Force Research Laboratory*, J. Kolis,* Clemson University*, J. Petrosky*, Air Force Institute of Technology

Analyses of depth- and temperature-resolved cathodoluminescence experimental techniques have identified many previously unobserved spectral characteristics in $U_xTh_{1-x}O_2$ compounds grown using a slow growth hydrothermal method. Three $U_xTh_{1-x}O_2$ (x = 0.00, 0.01, 0.22) hydrothermally grown, single crystals were examined using cathodoluminescence. Unique luminescence features were identified as a function of uranium concentration. In the undoped and x = 0.01 $U_xTh_{1-x}O_2$, an electronic phase transition is observed as a 20 nm (0.21 eV) red-shift in the wavelength of maximum emission. This red-shift appears when the crystals are heated during both 5 and 10 keV electron beam irradiation. Conversely, a similar phase transition is not observed in the $U_xTh_{1-x}O_2$ alloy (x = 0.22). Instead, the wavelength of maximum emission remains constant at 305 nm (4.07 eV). Ultimately, the addition of uranium to the ThO_2 lattice increases the band gap of the material which is identified as a 10 nm (0.13 eV) blue shift if the luminescence. Finally, a quadrupole transition is observed in the uranium-containing crystals (O 2p to U 5f) at approximately 600 nm (2.07 eV).

Surface Science
Room: 309 - Session SS+AS+EN-MoM

Mechanistic Insights into Surface Reactions: Catalysis, ALD, etc.
Moderator: Falko Netzer, University of Graz, Junseok Lee, National Energy Technology Laboratory

8:20am **SS+AS+EN-MoM1 Electron Trap or Atomic Hydrogen Recombination Catalyst? The Role of Metals in Photocatalysis Revisited**, *J.-B. Joo, R.J. Dillon, I. Lee, C.J. Bardeen,* ***Francisco Zaera***, University of California - Riverside **INVITED**

The production of hydrogen from water with semiconductor photocatalysts is often promoted by the addition of a small amount of a metal to their surfaces. It is commonly believed that the resulting enhancement in catalytic activity is due to a fast transfer of the excited electrons generated by photon absorption from the semiconductor to the metal, a step that prevents de-excitation back to the ground electronic state. Here we provide several pieces of evidence to argue against this mechanism. An alternative explanation is advanced where the metal acts as a catalyst for the recombination of the hydrogen atoms made via the reduction of protons on the surface of the semiconductor instead. New metal@TiO_2 yolk-shell nanomaterials were conceived to test our hypothesis, and the preparation and characterization of those will be discussed in this presentation as well.

9:00am **SS+AS+EN-MoM3 Atomically Resolved Observation of Defects Catalysing Phase Transitions in an Adsorbate System**, *M. Cordin, B.A.J. Lechner, S. Duerrbeck, A. Menzel,* ***Erminald Bertel***, University of Innsbruck, Austria, *J. Redinger,* Vienna University of Technology, Austria, *C. Franchini*, University of Vienna, Austria

First order phase transitions exhibit a nucleation barrier. Normally, the barrier is lowered by heterogeneous nucleation at interfaces or extrinsic defects. Homogeneous nucleation, in contrast, is strongly activated and results in a significant hysteresis. Molecular dynamics calculations have suggested that an important step in homogeneous nucleation involves the formation and subsequent separation of defect pairs[1-2].

Here we report a (2x1)→c(2x2) order-order phase transition in a two-dimensional (2D) adsorbate system (Br/Pt(110) at 0.5 monolayer coverage) as a function of temperature[3]. Although an order-order phase transition is first-order according to Landau rules, the present system exhibits strong fluctuations within a wide temperature range (50K-250K). At 50 K the fluctuations are sluggish enough to allow atomically resolved observation of the phase conversion mechanism by temperature-variable Scanning Tunneling Microscopy. The transition is heralded by local density fluctuations in the adsorbate. The density variation consists of a compression (soliton) and a dilution (anti-soliton). At the transition temperature the two defect moieties are able to separate and travel independently through the system, thereby converting one phase into the other. Away from the transition temperature, separation of the defect pair would create the “wrong” phase, thus increasing the free energy of the system. This is equivalent to an effective attractive interaction between soliton and anti-soliton, in close analogy to the string interaction in spin systems[4]. The one-to-one correspondence can be made transparent by introducing a pseudo-spin variable, i.e. an occupation number +/-1 assigned to every bonding site. The defect-pair separation mechanism partially circumvents the nucleation barrier and thus promotes fluctuations, particularly in low-dimensional systems.

Defect-pair separation as a key step in phase transitions is a concept which arose from the analysis of molecular dynamics calculations. To our knowledge, the present study represents the first direct experimental observation with atomic resolution of such a mechanism. Furthermore, it illustrates the important role of the string interaction in suppressing fluctuations, which is very efficient in 3D systems, weaker in 2D systems and totally absent in 1D.

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9:20am **SS+AS+EN-MoM4 The Co-adsorption of Water and ammonia on Pt(111)**, *B.A.J. Lechner,* Lawrence Berkeley National Laboratory, *Y. Kim, H. Kang,* Seoul National University, Korea, ***Miquel Salmeron***, Lawrence Berkeley National Laboratory

Water (H_2O) and ammonia (NH_3) are arguably the most important inorganic molecules in the chemical industry. Both have the ability to form hydrogen bonds and mix readily in the liquid form. However, upon adsorption onto a metal surface, the molecules can form fewer yet more directional hydrogen bonds. To investigate the interaction between these two species at the molecular level we present a scanning tunneling microscopy (STM) study of the co-adsorption of water and ammonia on Pt(111), a substrate which bonds both molecules strongly but does not promote their decomposition.

Prior investigations have suggested the formation of the ammonium ion, NH_4^+, upon adsorption of ammonia onto a water monolayer on Ru(0001) [1], implying that the two molecules react readily when adsorbed on transition metal surfaces. Furthermore, a theoretical study of the co-adsorption of ammonia and water on Cu(110) proposed an intimately mixed layer of ammonia and water as the energetically most favorable structure [2].

Here, we present the first microscopic investigation of co-adsorbed water and ammonia species. Upon adsorption at 4 K, ammonia and water form disordered structures, yet as the temperature is increased the two species segregate on the substrate. Indeed, at temperatures above 77 K, ammonia invariably prefers to bond to the Pt surface and only adsorbs on a water film once the monolayer is complete and no active sites remain on the substrate. When adsorbed on the water layer, we find that ammonia bonds to the water molecules that are lifted off the substrate due to a lattice mismatch of the water monolayer and the Pt(111) geometry, which we believe is due to their ability to provide a hydrogen atom for the hydrogen bond more readily than the molecules bonded more strongly to the substrate.

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9:40am **SS+AS+EN-MoM5 Thermal Decomposition of Ethylene on Ru(001)**, ***Yuan Ren***, *I. Waluyo, M. Trenary*, University of Illinois at Chicago

Ruthenium is an important catalyst in the Fischer-Tropsch process which deals with the conversion of syngas (CO and H_2) into hydrocarbons. One of the most important aspects in the Fischer-Tropsch reaction is the chain growth from a C_1 species to longer chain hydrocarbons. It is, therefore, important to study the chemistry of various C_xH_y hydrocarbon fragments on transition metal surfaces as building blocks in the chain growth mechanism. Ethylidyne (CCH_3) is an interesting hydrocarbon fragment that has been studied on many surfaces as the decomposition product of ethylene. Although the formation of ethylidyne on Ru(001) from the dehydrogenation of ethylene has been studied using high resolution electron energy loss spectroscopy (HREELS) and reflection absorption infrared spectroscopy (RAIRS) in the past, there is a lack of agreement in the literature about the mechanism of ethylene decomposition.

In this study, reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD) were used to characterize and identify the surface intermediates formed in the thermal decomposition of ethylene (C_2H_4) on Ru(001). Ethylene is found to adsorb to the surface in a di-σ bonded complex at 95 K and dehydrogenates to form ethylidyne (CCH_3) above 150 K. Upon further annealing the crystal to above 300 K, ethylidyne dehydrogenates to ethynyl (CCH). Annealing to higher than 450 K causes ethynyl to decompose to methylidyne (CH).The characterization of surface intermediates provides us with more insights into the thermal decomposition of ethylene on Ru(001), which is essential to reveal the reaction mechanism.

10:00am **SS+AS+EN-MoM6 Kinetics of Alkyl Species on Pt(111)**, ***Yifeng Song***, *I.A. Harrison*, University of Virginia

Kinetics of Alkyl Species on Pt(111)

Yifeng Song and Ian Harrison

University of Virginia

Charlottesville, VA 22904

A heated effusive molecular beam was used to dose hot alkanes on to a relatively cold Pt(111) surface to overcome the initial activation barrier for dissociative chemisorption and to trap reactive intermediate species on the surface for subsequent spectroscopic and kinetic studies. Both reflection absorption infrared spectroscopy (RAIRS) and temperature programmed reaction (TPR) techniques were employed, in a complimentary way, to investigate the kinetics of alkyl fragments. Particular attention was paid to methylidyne (-CH) decomposition kinetics, which have been proposed to be potentially rate-limiting in catalytic steam reforming of methane according to recent DFT calculations. Comparison between reforming kinetics of single crystal surfaces and nanocatalysts are made. Elementary steps including the cleavage and formation of C-H and C-C bonds within other C1, C2 and C3 reactive intermediates were also studied. The experimental findings, together with some theoretical work, provide molecularly resolved information relevant to catalytic reforming of light alkanes.

10:40am **SS+AS+EN-MoM8 C_2 Hydrogenation at Ambient Pressure on Pt(111)**, ***Joel Krooswyk***, *M. Trenary*, University of Illinois at Chicago

Carbon has been shown to be the decomposition product from catalytic reactions involving hydrocarbons adsorbed on metal catalysts. Its presence reduces the amount of active surface sites available during a reaction. The decomposition products from adsorbed acetylene and ethylene on Pt(111) are C_2 and C_1 species, respectively. A previous UHV study showed that C_2H_2 adsorbed on Pt(111) at 750 K immediately decomposes to mostly C_2 species. H_2 was then coadsorbed with C_2 at 85 K and annealed to 400 K, which produced ethylidyne (CCH_3), ethynyl (CCH), and methylidyne (CH) species. None of the species were hydrogenated to ethylene or ethane, and after annealing to 750 K, a percentage of the carbon on the surface could be rehydrogenated after cooling the crystal to 300 K and coadsorbing H_2.

In this study, the hydrogenation of C_2 species in 1×10^{-2} to 1 Torr of H_2 was monitored with RAIRS. The species was created on Pt(111) with C_2H_2 adsorption at 750 K as done previously and the crystal was cooled to 300 K. The crystal was then annealed in an ambient pressure of H_2. The C_2 species are hydrogenated to ethylidyne at 400 K and then to ethane at approximately 450-500 K. This reaction is shown to be dependent on the pressure of H_2. The results show that ethylidyne will be hydrogenated at 450 and 500 K at 1.0 and 1×10^{-2} Torr H_2, respectively. To show that the C_2 species are fully hydrogenated and desorbed as ethane, which indicates that the surface is clean, CO was leaked into the cell with H_2. We observe after the 500 K anneal that the peak assigned to the CO species is similar in intensity to one from CO adsorbed on a clean surface. This indicates that there are no C_2 species remaining on the surface. Also, the peak positions of the terminal and bridge sites are shifted, which indicates that there is a high coverage of H atoms adsorbed on the surface.

11:00am **SS+AS+EN-MoM9 Reaction Kinetics and Mechanism between Nitrate Radicals and Functionalized Organic Surfaces**, ***Yafen Zhang***, *J.R. Morris*, Virginia Tech

Interfacial reactions of nitrate radicals (NO_3) with organic surfaces play an important role in atmospheric chemistry. To gain insight into the kinetic and mechanic details, reactions between gas-phase nitrate radicals and model organic surfaces have been investigated. The experimental approach employs *in situ* reflection-absorption infrared spectroscopy (RAIRS) to monitor bond rupture and formation while a well-characterized effusive flux of NO_3 impinges on the organic surface. Model surfaces are created by the spontaneous adsorption of either vinyl-terminated alkanethiols ($HS(CH_2)_{16}CHCH_2$) or hydroxyl-terminated alkanthiols ($HS(CH_2)_{16}OH$) onto a polycrystalline gold substrate. The $H_2C{=}CH$-terminated self-assembled monolayers (SAMs) provide a well-defined surface with the double bond positioned precisely at the gas-surface interface. The surface reaction kinetics obtained from RAIRS revealed that the consumption rate of the terminal vinyl groups is nearly identical to the formation rate of a surface-bound nitrate species and implies that the mechanism is one of direct addition to the vinyl group rather than hydrogen abstraction. Upon nitrate radical collisions with the surface, the initial reaction probability for consumption of carbon-carbon double bonds was determined to be (2.3 ± 0.5) X 10^{-3}. This rate is approximately two orders of magnitude greater than the rate of ozone reactions on the same surface, which suggests that oxidation of surface-bound vinyl groups by nighttime nitrate radicals may play an important role in atmospheric chemistry despite their relatively low concentration. In addition to studies involving the $H_2C{=}CH$-terminated SAMs, we have probed the reaction dynamics of NO_3 on HO-terminated SAMs. These experiments have revealed that the polarity of the terminal group has a large effect on the interfacial reaction rates. For the HO-terminated SAMs, the initial reaction probability was determined to be (5.5 ± 0.6) X 10^{-3} and the reaction mechanism appears to involve efficient hydrogen abstraction at the methylene group adjacent to hydroxyl terminus.

11:20am **SS+AS+EN-MoM10 Oxide Growth Kinetics at Sio2/si(001) Interfaces Induced by Rapid Temperature Raising**, ***Shuichi Ogawa***, *J. Tang*, Tohoku University, Japan, *A. Yoshigoe*, JAEA, Japan, *K. Nishimoto*, Tohoku University, Japan, *S. Ishidzuka*, Akita Nat. Col. Technol., Japan, *Y. Teraoka*, JAEA, Japan, *Y. Takakuwa*, Tohoku University, Japan

Thermal oxidation of Si is widely used in the fabrication of electric devices and MEMS. In the recent process, rapid thermal annealing (RTA) is used in a thermal oxidation process. In the RTA process, the temperature changes during the oxidation, but the temperature changing effects in the oxidation rate have not been cleared yet. In this study, the dependence of interface oxidation kinetics on the temperature was investigated by real-time RHEED combined with AES to measure the oxide growth rate. Based on the activation energy and pre-exponential factor of the interface oxidation at SiO_2/Si(001) interface, the rate-limiting reaction of the interface oxidation is discussed.

The oxidation experiments were performed with an apparatus equipped with facilities of RHEED combined with AES (Tohoku Univ.), and chemical bonding states including not only suboxide components but also strained Si atoms were investigated XPS at BL23SU, SPring-8. The clean Si(001) surfaces were oxidized by dry O_2 gas at initial temperature T_1. When the clean surfaces were completely oxidized, the temperature was rised from T_1 to T_2. T_1 was changed between room temperature (RT) and 561 °C.

When temperature was rised from T_1 to T_2, the interface oxidation is enhanced. The initial oxidation rate after rising temperature k_2 is discussed in this study. The k_2 strongly correlates to the difference of T_1 and T_2. The Arrhenius equations between k_2 and T_2 are obtained in various T_1. As the result, activation energy is obtained as 0.27 eV in good agreement with the previous experimental result[1] and theoretical study[2]. In addition, it is found that activation energy is independent from T_1. On the other hand, pre-exponential factor decreases with increasing T_1, decreasing by about one order when T_1 increases from RT to 561 °C. In the XPS results, the Si^{4+} component increases and suboxide components and strained Si components (Si^{α} and Si^{β})[3] decrease with temperature elevation from 300 to 600 °C.

Based on these results, we propose the reaction between point defects (emitted Si atoms and its vacancies) generated by the oxidation-induced strain and O_2 molecules as the rate-limiting reaction of the interface oxidation.

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[2] H. Kageshima et al, Jpn. J. Appl. Phys. 45 (2006) 7672.

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11:40am **SS+AS+EN-MoM11 Electron Beam Induced Surface Reactions of Adsorbed π-allyl Ruthenium Tricarbonyl Bromide: Towards the Design of Precursors Specifically for Electron Beam Induced Deposition**, ***Julie Spencer***, Johns Hopkins University, *R.G. Thorman,* University of Iceland, *M.S. Barclay,* Johns Hopkins University, *J.A. Brannaka,* University of Florida, *O. Ingólfsson,* University of Iceland, *L. McElwee-White,* University of Florida, *D.H. Fairbrother*, Johns Hopkins University

This surface science study focuses on elucidating the electron stimulated elementary reactions involved in Electron Beam Induced Deposition (EBID) of π-allyl ruthenium tricarbonyl bromide (π-$C_3H_5Ru(CO)_3Br$), an organometallic precursor synthesized specifically to test its suitability as an EBID precursor. EBID is a minimally invasive, resistless lithographic process which uses the electron stimulated decomposition of volatile organometallics under low vacuum conditions to fabricate and prototype three-dimensional metallic nanostructures. To date, EBID of nanostructures has used precursors designed for thermal processes, such as chemical vapor deposition (CVD). However, precursors that yield pure metal deposits in CVD often create EBID deposits with high levels of organic contamination which severely limits the range of potential applications for EBID nanostructures, highlighting the need to better understand how the structure of organometallics influences their electron stimulated reactions. To address this knowledge gap we have conducted ultra-high vacuum (UHV) surface science studies to probe the effects of 500eV electrons on nanometer scale films of organometallics adsorbed on inert substrates at low temperatures using X-ray Photoelectron Spectrometry and Mass spectrometry. Recently, we have collaborated with synthetic organometallic chemists to study organometallic complexes not designed for CVD to test specific hypotheses about how the EBID process occurs; the first example of this new collaboration is π-allyl ruthenium tricarbonyl bromide (π-$C_3H_5Ru(CO)_3Br$). Experimental results indicate that electron stimulated decomposition of π-$C_3H_5Ru(CO)_3Br$ causes the central Ru atom to become reduced and in the process causes the vast majority of the carbonyl ligands to be ejected into the gas phase, with no loss of Br or the carbon atoms in the π-allyl ligand. A parallel study of π-$C_3H_5Ru(CO)_3Cl$ indicated that the identity of the halogen does not affect the decomposition process. However, although halogen atoms are not labile in the initial decomposition step, they can be removed by a slower electron stimulated desorption process at higher electron fluxes more representative of those encountered in typical EBID experiments which are conducted in electron microscopes. Collectively, these results suggest that organometallic precursors whose ligand architecture contains a combination of carbonyl and halogen ligands could be used to create EBID deposits with higher metal contents than are currently possible. To test this hypothesis we will also present results on the behavior of cis-dicarbonyldichloro platinum(II), *cis*-$PtCl_2(CO)_2$.

Surface Science
Room: 315 - Session SS+EN-MoM

Photocatalysis and Photochemistry at Surfaces
Moderator: Andrew Gellman, Carnegie Mellon University, Bruce Koel, Princeton University

8:20am **SS+EN-MoM1 Reaction Chemistry at Surfaces of Hematite-Based Photoelectrocatalysts**, *P. Zhao, C. Kronawitter, **Bruce Koel***, Princeton University

Hematite (α-Fe_2O_3)-based photoanodes are promising materials for photoelectrochemical hydrogen generation. We report on fundamental studies of surface structure and reaction chemistry associated with the heterogeneous oxidation of water on such materials by applying a classical surface science approach. We have characterized the structure and properties of Ni-doped and mixed-oxide hematite surfaces formed by vapor deposition under controlled conditions utilizing a range of techniques for surface analysis. The structure of Ni-modified thin films of α-Fe_2O_3 model catalysts with different morphology and geometry was characterized by LEED and STM. Then, water adsorption and reaction were studied by TPD, XPS, UPS, and vibrational spectroscopy by HREELS, characterizing the influence of Ni-modification on thermal and photochemical reaction mechanisms. Ni doping is found to be associated with a new termination for the α-Fe_2O_3(0001) film. Water TPD shows that Ni doping induces new surface chemistry, as revealed by a new, higher temperature OH recombination desorption peak, which is due to more stable surface-bound OH groups as identified by UPS. These surface-science type experiments were combined with photoelectrochemical water oxidation measurements on photoanodes prepared by thin-film and nano-materials synthesis to elucidate new information on the surface phases of hematite-based photoanodes and about their specific stability and reactivity toward photoelectrochemical water splitting.

This work was supported by the Addy/ISN North American Low Carbon Emission Energy Self-Sufficiency Fund of the Andlinger Center for Energy and the Environment (ACEE) and by the Grand Challenges Program at Princeton University.

8:40am **SS+EN-MoM2 Infrared Reflection-Absorption Spectroscopy Study of Adsorption and Photo-Decomposition of Formic Acid on Reduced and Defective Rutile TiO_2 (110) Surfaces**, ***Andreas Mattsson**, L. Österlund*, Uppsala University, Sweden

Adsorption and photo-decomposition of formic acid on rutile TiO_2(110) have been investigated with infrared reflection-absorption spectroscopy (IRRAS) employing p- and s-polarized light along the [001] and [1-10] crystal directions. The single crystal surfaces were prepared either by sputtering and annealing in ultra-high vacuum (UHV) to obtain a reduced surface (r-TiO_2), or by sputtering alone to create a rough, highly defective surface (sp-TiO_2). Results are compared with corresponding measurements in synthetic air on rutile nanocrystals performed. IRRAS spectra obtained on r-TiO_2 and rutile nanocrystals are very similar (Fig. S1), and show that in both cases formic acid dissociates and is predominately adsorbed as a bridging bidentate formate species,[1] demonstrating that the adsorption structure on the nanocrystals is determined by interactions with majority (110) surfaces. In contrast, the IRRAS spectra on sp-TiO_2 are different (Fig. S1), with only minor spectral features associated with (110) surfaces, which can be explained by changed adsorption geometry due to bonding to low-coordinated Ti^{3+} atoms. IRRAS measurements in UHV on thin nanoporous rutile films, made by reactive DC sputtering, were performed to compare the adsorption geometry of formate with that for single crystal surfaces and nanoparticles. The UV-induced rate of formate photo-decomposition is about 30 times higher on rutile nanocrystals in synthetic air compared with sp-TiO_2 under UHV conditions, and even larger than on r-TiO_2.[2] These differences are explained by the lack of oxygen and limited hydroxyl coverage under UHV conditions (thus quenching electron scavenging by adsorbed O_2 and lowering OH radical formation), and by strong bonding of formate on (110) surfaces which lowers the reactivity on r-TiO_2 further. Our results suggest that surface reaction studies of formic acid conducted at elevated pressures on rutile nanocrystals can be accurately modelled with single crystal studies conducted in UHV.

[1] A. Mattsson, S-L. Hu, K, Hermansson, L. Österlund, Journal of Chemical Physics 140 (2014) 034705

[2] L. Österlund, Solid State Phenomena 162 (2010) 203-219

9:00am **SS+EN-MoM3 Molecular Beam Epitaxy of Highly Mismatched GaN Alloys with GaAs, GaSb and GaBi for Potential Water Splitting and Other Solar Energy Conversion Applications**, ***Sergei Novikov***, University of Nottingham, UK, *K.M. Yu,* Lawrence Berkeley National Laboratory, *W.L. Sarney,* US Army Research Laboratory, *Z. Liliental-Weber,* Lawrence Berkeley National Laboratory, *R.W. Martin,* University of Strathclyde, UK, *S.P. Svensson,* US Army Research Laboratory, *W. Walukiewicz,* Lawrence Berkeley National Laboratory, *C.T. Foxon*, University of Nottingham, UK **INVITED**

We have grown GaN layers alloyed with GaAs, GaSb and GaBi compounds using plasma-assisted molecular beam epitaxy (PA-MBE) and extensively characterized their structural, optical and electrical properties.

Electronic band structures of these so-called highly mismatched alloys (HMAs) are described by the band anticrossing (BAC) model which predicts that the alloys should exhibit a wide range of direct energy gaps. We have shown previously that the energy gap of $GaN_{1-x}As_x$ alloys varies from 0.7eV to 3.4eV. An even larger modification of the band structures is anticipated for more extremely mismatched $GaN_{1-x}Sb_x$ and $GaN_{1-x}Bi_x$ alloys. The large band gap range and controllable conduction and valence band edge positions makes the HMAs promising materials for efficient solar energy conversion devices. For example, these HMAs may be suitable for solar water splitting applications for hydrogen production. As efficient photoelectrodes, the bandgap of the semiconductor must be >2 eV to induce electrochemical decomposition of water but still small enough to absorb a significant portion of the solar spectrum. In addition the band edges must also straddle the H_2O redox potentials.

At dilute doping levels, substitutions of As, Sb and Bi into the N sublattice results in formation of localized energy levels above the valence band in GaN. Our measurements on GaN doped with As and Sb have demonstrated that the As and the Sb impurity levels lie at about 0.7eV and 1.2eV above the valence band edge of GaN, respectively.

The BAC model predicts that at a higher concentration of the group V elements the interaction of the impurity levels with the extended states of the valence band leads to formation of an impurity-derived, fully occupied narrow band that plays a role of the new valence band edge. This results in an abrupt upward shift of the valence band edge and a reduction of the optical gap of the HMAs. We have achieved the enhanced incorporation of As, Sb and Bi by growing the layers at extremely low temperatures (down to about 100^{o}C). Although the layers become amorphous for high As, Sb and Bi content, the measured composition dependence of the optical absorption edge are consistent with the predictions of the BAC model, indicating that the amorphous HMAs samples have a short-range order resembling random crystalline alloys. The large band gap range and controllable positions of the conduction and valence bands make these HMAs promising materials for efficient solar energy conversion devices.

9:40am **SS+EN-MoM5 Photochemistry of Acetone on Reduced Rutile TiO_2(110)**, ***Nikolay Petrik**, M.A. Henderson, G.A. Kimmel*, Pacific Northwest National Laboratory

TiO_2 is an important photocatalyst with many practical applications. However, fundamental understanding of thermal and non-thermal reactions on TiO_2 surfaces is still lacking. We have investigated the ultraviolet (UV) photon-stimulated reactions acetone and oxygen adsorbed on reduced rutile TiO_2(110). Previous research suggests that a thermal reaction between acetone and chemisorbed oxygen forms acetone diolate – a photochemically active product.[1] During UV irradiation, a methyl radical is ejected leaving acetate on the surface. Using infrared reflection absorption spectroscopy, we have identified the acetone diolate, which degrades during UV irradiation forming a new product. We have also measured the angular distribution of the photodesorbing methyl radicals, which is consistent with their ejection from the acetone diolate. Specifically, a peak in the distribution near ~60° to the surface normal is detected in the plane perpendicular to the BBO rows. However, we have also observed a second channel for photo-ejection of methyl radical for larger acetone:O_2 ratios. It manifests itself with a photodesorption peak normal to the surface and slower signal decay kinetics. These studies provide new insights into mechanisms responsible for the photochemistry of small molecules on TiO_2 and other oxide surfaces. This work was supported by the US Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences & Biosciences. The work was performed using EMSL, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory (PNNL) . PNNL is a multiprogram national laboratory operated for DOE by Battelle under Contract DE-AC05-76RL01830 .

(1) Henderson, M. A. Relationship of O_2 Photodesorption in Photooxidation of Acetone on TiO_2 . *J. Phys. Chem. C*, 2008 ,112, 11433-11440.

10:00am **SS+EN-MoM6 STM Spectroscopic Studies of TMAA Photocatalysis on TiO_2**, ***Denis Potapenko***, *Z. Li, R.M. Osgood*, Columbia University

Titanium oxide is a versatile photocatalytic material and it has been the subject of much research throughout the last two decades. 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 tri-methyl 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 the present work we combine three methods of initiation of surface chemistry: a) excitation of charge carriers in bulk TiO_2 with monochromated light from a UV-vis lamp, b) injection of the charge carriers from the STM tip directly into an adsorbed molecule, and c) injection of hot carriers into the substrate from the STM tip. In the latter case the surface reactions are initiated in the vicinity of the injection point by the electrical charges diffusing in the bulk of TiO_2, thus giving a unique insight into the charge dynamics. 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-decomposition.

11:00am **SS+EN-MoM9 Photoluminescence Response of p-$GaInP_2$ Photocathodes to Vapor and Solution Ambients**, ***James Young***, University of Colorado, Boulder, *H. Doscher, T.G. Deutsch, J.A. Turner,* National Renewable Energy Laboratory, *S.M. George*, University of Colorado, Boulder

III-V photoelectrochemical (PEC) devices have achieved high solar-to-hydrogen water splitting efficiencies but corrosion greatly limits their operating lifetime. A dynamic three-phase semiconductor-electrolyte-hydrogen (oxygen) system exists at a photocathode (photoanode) surface during operation. Understanding the interaction of water, hydrogen, and oxygen with III-V surfaces is critical to optimizing device performance and applying corrosion-resistant surface modifications. In this work, we use photoluminescence (PL) to probe the surface response of p-type $GaInP_2$ to several gas and solution ambients *in-situ*. X-ray photoelectron spectroscopy and photoelectrochemical techniques are used to characterize surface changes *ex-situ*. Pretreating p-$GaInP_2$ with sulfuric acid removes surface oxide and doubles p-$GaInP_2$ band-to-band PL yield when measured in air. Measurements in vacuum show that PL of pretreated samples increases reversibly with adsorption isotherm dependence on water vapor at partial pressures below 2 Torr while samples without the pretreatment show no PL response to water vapor. A comparison of water to other vapor phase ambients suggests that PL response increases with the dipole strength and involves dissociative adsorption. In oxygen ambient, the PL decays irreversibly which we attribute to photo-oxidation of the p-$GaInP_2$ surface. We will also present results from measurements in hydrogen ambient and PL measurements and monitoring in electrolyte solutions with a discussion of their relevance to PEC device performance and usefulness in characterizing corrosion resistant surface modifications.

Monday Afternoon, November 10, 2014

2D Materials Focus Topic
Room: 310 - Session 2D+AS+EM+NS+SS-MoA

Dopants, Defects, and Interfaces in 2D Materials
Moderator: Jun Lou, Rice University

2:00pm **2D+AS+EM+NS+SS-MoA1 Cutting and Assembling 2 Nanometer Voids in Single Layer Hexagonal Boron Nitride**, ***Thomas Greber***, *H.Y. Cun, M. Iannuzzi, A. Hemmi, J. Osterwalder*, University of Zurich, Switzerland **INVITED**

Argon implantation beneath hexagonal boron nitride nanomesh on Rh(111) [1] leads to the formation of vacancy and interstitial defects [2]. The nanomesh is a single layer of hexagonal boron nitride on Rh(111), where 13x13 h-BN units accommodate on 12x12 Rh unit cells. The resulting super-honeycomb has a lattice constant of 3.2 nm and consists in regions where the h-BN "wets" the Rh substrate (pores), and regions where h-BN is quasi freestanding (wires) [3].

The interstitial defects are called "nanotents", where atoms are trapped beneath the ultimately thin "rainfly" made of a single layer of h-BN [2,4]. They are stable at room temperature and survive exposure to air.

The vacancy defects are sites where a boron or a nitrogen atom was kicked out by the Ar ion impact. If the implanted structures are annealed to 900 K the can-opener effect occurs: 2 nm h-BN-flakes or "lids" are cut out of the h-BN nanomesh and 2 nm voids form [2]. At higher temperatures the resulting voids may diffuse and assemble, due to their repulsive interaction, in a super-superstructure with some order, i.e., a nearest neighbor distance of about 15 nm. Near the disintegration temperature of the h-BN nanomesh we finally observe self-healing of the voids in the nanomesh, which we assign to their annihilation in larger holes in the structure.

The report bases on scanning tunneling microscopy, x-ray photoelectron spectroscopy, molecular dynamics and density functional theory calculations.

Financial support by the Swiss National Science Foundation and support by the EC under the Graphene Flagship (contract no. CNECT-ICT-604391) is gratefully acknowledged. We thank the Swiss National Supercomputer Centre (CSCS) for allocation of computer time.

[1] M. Corso et al. Science, 303 (2004) 217.

[2] H. Y. Cun et al. Nano Letters 13 (2013) 2098.

[3] S. Berner et al. Angew. Chem. Int. Ed. 46 (2007) 5115.

[4] H.Y. Cun et al. ACS Nano 8 (2014) 1014.

2:40pm **2D+AS+EM+NS+SS-MoA3 Engineering Structural Defects in Graphene Materials**, ***Jeremy Robinson***, *M. Zalalutdinov, J. Culbertson, C. Junkermier, P.E. Sheehan, T. Reinecke, A. Friedman*, Naval Research Laboratory

Graphene's atomic thinness makes it highly sensitive to surface adsorbates or defects within its carbon backbone. Aside from the known effects and impact on electronic properties, here we demonstrate the impact of defects on the mechanical properties and the response of mechanical resonators. In particular, once defects are formed in atomically-thin materials they can be quite mobile and form more complicated defect structures such as bi- or tetra-vacancy clusters. We execute experiments using mechanical drum resonators made from single- to multi- to many-layer graphene systems. We use both CVD grown graphene and reduced graphene oxide (rGO) films to capture a wide range of defect structures. By measuring the fundamental frequency response of the resonators (in the MHz range) we extract properties such as tension, quality factor, and modulus as a function of external manipulation [1]. For highly defective rGO films measuring 10-40nm thick, we can tune the frequency response by 500% and quality factor by 20x through laser annealing, which effectively rearranges defects throughout the film [1]. Alternatively, using graphene 1-4 layers thick, we find the resonator response is significantly more sensitive to the formation and annihilation of meta-stable defects, such as the tetra-vacancy structure. We will show how the defect mobility and resonator response changes with different energy photons and come to understand these differences based on calculated defect migration energies of different defects types in graphene.

[1] *Nano Letters***12**, 4212 (2012)

3:00pm **2D+AS+EM+NS+SS-MoA4 Graphene Cleaning using a Low Energy Ar Ion Beam**, ***KiSeok Kim***, *G. Yeom*, Sungkyunkwan University, Republic of Korea

Recently, graphene has been widely investigated due to the superior electrical, mechanical, thermal, and chemical properties. Especially, CVD graphene which was grown on Cu foil and transferred to various substrates using PMMA has been used most widely due to the possible large area applications such as electronic devices for displays, semiconductors, etc. However, in order to apply the transferred CVD graphene to the various electronic device fabrication, PMMA residue on the graphene surface formed during the transfer process and lithography process needs to be completely removed without damage. Various methods have been investigated to remove the residue on the graphene surface such as current cleaning, heat treatment, chemical cleaning, etc. However, it is reported that these methods are not effective in removing the residue on graphene or not applicable to industry.

In this study, a controlled Ar ion beam has been used to effectively remove the PMMA residue on graphene surface. By controlling the Ar ion beam condition, the residue on graphene surface could be removed while minimizing the damage on the graphene surface. Especially, by lowering the Ar beam energy less than 10 eV, it was possible to effectively remove the PMMA residue without damaging the graphene. The removal of PMMA residue on the graphene surface could be identified using Raman Spectroscopy showing the red shift of 2D peak (2670 cm^{-1}) and blue shift of G peak (1580 cm^{-1}) in addition to the decrease of RMS roughness from 1.3nm to 0.3 nm using an AFM (Atomic Force Microscopy). The effectiveness of graphene cleaning was also confirmed by XPS (X-ray Photoelectron Spectroscopy), by the uniform deposition of ALD HfO_2 layer on the cleaned graphene surface, by measuring the electrical properties of deposited ALD HfO_2, etc.

3:40pm **2D+AS+EM+NS+SS-MoA6 Electronic Structure Modification in van der Waals Heterostructures: Interlayer Hybridization in the Case of Graphene/MoS2**, ***Matthias Batzill***, *H. Coy-Diaz,* University of South Florida*, M.C. Asensio,* Synchrotron Soleil, France*, J. Avila*, Synchrotron Soleil

Artificial van der Waals heterostructures promise to combine materials with diverse properties. Simple mechanical stacking or conventional growth of molecular hetero-layers would enable fabrication of novel materials or device-structures with atomically precise interfaces. Because covalent bonding in these layered materials is limited to molecular-planes, interface interactions between dissimilar materials are expected to modify the properties of the individual layers only weakly. Here we prepare graphene/MoS_2 heterostuctures by transferring CVD-grown graphene onto a MoS_2 substrate. It is shown that high quality interfaces between graphene and MoS_2 can be obtained by UHV annealing . The quality of the graphene is demonstrated by atomic resolution scanning tunneling microscopy of ultraflat graphene. The electronic structure of the interface between the polycrystalline graphene and a MoS_2 substrate is measured by angle resolved photoemission spectroscopy (ARPES) and nano-ARPES utilizing a focused photon beam at the SOLEIL synchrotron. We show that at the Fermi-level graphene exhibits a perfect, gapless and undoped Dirac-cone. However, in regions where the π-band of graphene overlaps with states of the MoS_2 substrate, opening of several band-gaps are observed. This demonstrates that the electronic properties in van der Waals heterostructures can be significantly modified by interlayer interaction and thus exemplifying opportunities for tuning materials properties of graphene and other 2D-materials by interfacing them with dissimilar van-der Waals materials.

4:00pm **2D+AS+EM+NS+SS-MoA7 Edge States and Exposure to Hydrogen of Silicon at the 2D Limit on Ag(111)***, A.J. Mannix, B.T. Kiraly,* Argonne National Laboratory*, M.C. Hersam,* Northwestern University, ***Nathan Guisinger***, Argonne National Laboratory

Chemical functionalization of atomically thin materials results in significant modifications to their electronic properties, which can be exploited in device applications. Compared to the chemical inertness of graphene, 2D silicon is expected to exhibit greater reactivity, and thus a greater amenability to chemical functionalization. Among potential functionalization chemistries, hydrogen termination is favored for its relative simplicity and proven efficacy with graphene and bulk Si surfaces. Using ultra-high vacuum (UHV) scanning tunneling microscopy (STM), we have studied the temperature-dependent effects of exposing 2D silicon platelets grown on Ag(111) to molecular and atomic hydrogen. At low doses, atomic hydrogen results in limited adsorption and temperature dependent etching. In the bulk, the formation of vacancies and extended etch pits is observed. In addition, edge states can play a critical role in the electronic properties of 2D materials. We have also examined at the atomic-scale the edges of 2D silicon platelets.

4:20pm **2D+AS+EM+NS+SS-MoA8 Chlorine Trap-Doping for Transparent, Conductive, Thermally Stable and Damage-Free Graphene**, ***Pham Viet Phuong***, *K.N. Kim, M.H. Jeon, K.S. Kim, G. Yeom*, Sungkyunkwan University, Republic of Korea

We propose a novel doping method of graphene by cyclic trap-doping with low energy chlorine adsorption. Low energy chlorine adsorption for graphene chlorination avoided defect (D-band) formation during doping by maintaining the π-bonding of the graphene, which affects conductivity. In addition, by trapping chlorine dopants between the graphene layers, the proposed doping method dramatically decreased the sheet resistance by ~88% at an optimized condition. Among the reported doping methods including chemical, plasma, photochemical methods etc., the proposed doping method is believed to be the most promising for producing graphene of extremely high transmittance, low sheet resistance, high thermal stability, and high flexibility for use in various flexible electronic devices. Results of angle resolved X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron spectroscopy (HR-TEM), Raman spectroscopy, ultraviolet-Visible spectroscopy (UV-Vis) and sheet resistance, showed that this method is also non-destructive and controllable. The sheet resistance of the doped tri-layer graphene was 70 Ω/sq at 94% transmittance, which was maintained for more than 6.5 h at 230°C. Moreover, the defect intensity of graphene was not increased during the cyclic trap-doping.

4:40pm **2D+AS+EM+NS+SS-MoA9 Modification of Graphene by Neutral Beam Irradiation and Edge Structure Analysis**, ***Takeru Okada***, *S. Samukawa*, Tohoku University, Japan

Since the discovery of single layer of Graphite, Graphene, a single layer of hexagonal carbon atoms, has attracted much attention and shown exciting specific properties. Graphene is a zero band gap semiconductor. Therefore band gap control is one of most important issue to apply for electronic device applications. In order to construct electronic devices with logic operation, both p- and n-type conductions and the control of the carrier density in an active channel are required. Doping with foreign atoms, such as N and B, has proven to be an effective way to modify the electronic properties of carbon related materials and extend their applications. In particular, nitrogen doping brings a carrier which could turn carbon nanotube into n-type semiconductors. It is also feasible to modify the electronic properties of Graphene. Although several doping methods have reported so far, process damages (defect generation) cause degradation of electronic properties.

In this paper, we introduce ultra-low damage neutral beam system which consists of a plasma and process chambers that are separated by a carbon aperture. Charged species and ultra-violet photon from the plasma can be effectively eliminated by the aperture. As a result, only the neutral beam arrives the surface of the sample at the substrate in the process chamber.

We used nitrogen gas for plasma generation and adopted multi-layer Graphene to investigate nitridation mechanism. Graphene multi-layer was irradiated by nitrogen neutral beam with controlled energy of 10 eV at room temperature. The surface modification was analyzed by x-ray photoelectron spectroscopy (XPS). XPS analysis indicated that the carbon atoms were substituted to nitrogen atom and atomic concentration of nitrogen reaches 15 %. Additionally, bonding state of C and N was found to depend on neutral beam irradiation time. Thus beam energy controlled neutral beam can selective nitridation of Graphene. Furthermore the doping density is estimated by Raman spectroscopy and result in 10^{12} [cm^2], which is enough to n-type doping of Graphene.

5:00pm **2D+AS+EM+NS+SS-MoA10 Growth Mechanism of Metal Clusters on a Graphene/Ru(0001) Template**, ***Shixuan Du***, *L.Z. Zhang*, Chinese Academy of Sciences, *W. Hofer*, University of Liverpool, UK, *H.-J. Gao*, Chinese Academy of Sciences

Metal nano-clusters have attracted considerable interest because of the potential applications in catalysis and information storage. Due to the soft nature of epitaxial graphene and the lattice mismatch between graphene and metal substrates periodic moiré patterns can be formed. A graphene/metal template, moiré template, can be used to grow dispersed metal nano-clusters with controllable size and shape, or metal clusters with large size and metal layers. However, how intrinsic properties of metal atoms and the moiré template influence the selective adsorption and the growth mode of metal clusters is still open to debate. A general rule, predicting the morphology of metal nano-clusters on a G/metal surface, important to guide experimenters, is still missing. Using first-principles calculations combined with scanning tunneling microscopy experiments, we investigated the adsorption configurations, electronic structures and the corresponding growth mechanism of several transition metal (TM) atoms (Pt, Ru, Ir, Ti, Pd, Au, Ag, and Cu) on a graphene/Ru(0001) moiré template (G/Ru(0001)) at low coverage. We find that Pt, Ru, Ir, and Ti selectively adsorb on the fcc region of G/Ru(0001) and form ordered dispersed metal nano-clusters. This behavior is due to the unoccupied *d* orbital of the TM atoms and the strong sp^3 hybridization of carbon atoms in the fcc region of G/Ru(0001). Pd, Au, Ag, and Cu form nonselective structures because of the fully occupied *d* orbital. This mechanism can be extended to metals on a graphene/Rh(111) template. By using Pt as an example, we provide a layer by layer growth path for Pt nano-clusters in the fcc region of the G/Ru(0001). The simulations agree well with the experimental observations. Moreover, they also provide guidance for the selection of suitable metal atoms to form ordered dispersed metal nano-clusters on similar templates.

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1. L.Z. Zhang *et al*. Advanced Materials Interfaces, accepted.
2. Y. Pan *et al*. Applied Physics Letter, 95, 093106 (2009)

Actinides and Rare Earths Focus Topic
Room: 301 - Session AC+AS+MI+SA+SS-MoA

Theoretical Modeling of f Electron Systems

Moderator: Ladislav Havela, Charles University, Czech Republic

2:00pm **AC+AS+MI+SA+SS-MoA1 Nonmagnetic Ground State of PuO_2**, ***Jindrich Kolorenc***, Academy of Sciences of the Czech Republic **INVITED**

The correlated band theory implemented as a combination of the local density approximation with the dynamical mean-field theory is applied to PuO_2. We obtain an insulating electronic structure consistent with the experimental photoemission spectra, and a nonmagnetic ground state that is characterized by a noninteger filling of the plutonium f shell ($n_f \approx 4.4$). Due to a sizable hybridization of the f shell with the p states of oxygen, the ground state is more complex than the four-electron Russell–Saunders $^5I_4$ manifold split by the crystal field. The dynamical mean-field theory, which in the present case can be schematically viewed as an extension of the crystal-field model with hybridization terms, improves the agreement between the theory and experiment for the magnetic susceptibility [1]. Encouraged by the good accuracy achieved for PuO_2 , we apply the theory to several other tetravalent actinide oxides.

[1] A. B. Shick, J. Kolorenč, L. Havela, T. Gouder, and R. Caciuffo, Phys. Rev. B **89**, 041109 (2014).

2:40pm **AC+AS+MI+SA+SS-MoA3 DMFT Modeling of Electronic Spectral Properties in Pu-based Actinides**, ***Jian-Xin Zhu***, Los Alamos National Laboratory **INVITED**

Plutonium-based materials have been studied for many years due to their importance in nuclear energy applications. Scientifically, these materials exhibit highly complex properties. Pu metal shows a significant volume expansion and anomalous magnetic properties; while Pu-115 (like $PuCoGa_5$) are found to be superconductors. These intriguing phenomena originate from the special location of Pu in the Periodic Table, which is at the boundary between the light actinides that have itinerant 5f electrons and the heavy actinides with localized 5f electrons. They call out the notion of strong correlation of 5f electrons. In this talk, I will present a study of the electronic structure of Pu metals and its 115 compounds in the framework of the combination of local density functional approximation and dynamical mean-field theory. In particular, the results on momentum-resolved spectral functions will be presented and be compared with those based on the LDA only. In addition, the effect of Pu 5f electron occupancy on the electronic structure of these systems will also be discussed. The test of these results by future angle-resolved photoemission spectroscopy measurements will give a stringent constraint on the theoretical approach.

3:40pm **AC+AS+MI+SA+SS-MoA6 The Evolution in Pu Nanocluster Electronic Structure: From Atomicity to Three-Dimensionality**, ***James Tobin***, *S.W. Yu, B.W. Chung*, Lawrence Livermore National Laboratory, *M.V. Ryzhkov*, Russian Academy of Science-Urals, *A. Mirmelstein*, Russian Federation Nuclear Lab (VNIITF)

The development of electronic structure in solid systems as a function of size has long been a subject of great interest and extensive scientific investigation. Experimentally, the transition, from nanoscale or mesoscopic to bulk behavior in metal clusters, was reported in 1981 by Mason and co-workers. Similarly, the evolution from two-dimensional to three-dimensional band structure in metal overlayers and the manifestation of nanoscale effects in compound semiconductor have also observed. In the area of actinide materials, the progress has been slowed by the limitations imposed by the highly radioactive, chemically toxic and pyrolytic nature of these materials. Havela and Gouder and colleagues performed investigations upon Plutonium (Pu) ultra-thin films, deposited in situ by means of a discharge-plasma, and Trelenberg and co-workers developed an approach using laser ablation of Uranium (U). Gas phase studies of actinides have also been pursued including atoms, molecules and reactions. Recent theoretical studies include UO_2 molecules, solid actinide oxides, and actinide carbide clusters. A new approach to cluster calculations has been taken in this study. Past cluster calculations were arranged in such a way that the central atom would exist in a bulk like environment. In calculations herein, it is expected that the central atom will be in the most bulk-like environment as well. However, just as in any finite size object, there will be variation of potential at the positions of symmetry non-equivalent atoms within the simulated cluster. Hence, averaging over all of the atoms in the cluster will give a measure of the effect of size. We will use this aspect of cluster calculations to investigate size related effects. Here, we report the result of the calculation of the electronic structure of clusters of Pu and their comparison to bulk spectroscopic results. Lawrence Livermore National Laboratory is operated by Lawrence Livermore National Security, LLC, for the U.S. Department of Energy, National Nuclear Security Administration under Contract No. DE-AC52- 07NA27344. Work at the RAS and VNIITF was supported in part by Contract B590089 between LLNL and VNIITF. The Advanced Light Source (ALS) in Berkeley and the Stanford Synchrotron Radiation Laboratory are supported

by the DOE Office of Science, Office of Basic Energy Science. For more detail see:M.V. Ryzhkov, A. Mirmelstein, S.-W. Yu, B.W. Chung and J.G. Tobin, "Probing Actinide Electronic Structure through Pu Cluster Calculations," Intl. J. Quantum Chem. **113**, 1957 (2013); COVER ARTICLE .

4:00pm **AC+AS+MI+SA+SS-MoA7 First-Principles Density Functional Theory Simulation on Rare-Earth-Based Oxides as Fast Oxygen Ion Conductors**, ***Mamoru Sakaue***, *M. Alaydrus, H. Kasai,* Osaka University, Japan, *T. Ishihara*, Kyushu University, Japan

Development of novel fast ion conductors is a crucial issue for realizing solid oxide fuel cells (SOFCs) which can operate in low temperatures. While yttria-stabilized zirconia (YSZ) had been well-studied both by experiments and theories, exploration of other types of materials retaining high ionic conductivities in lower temperatures is still desired. Experimental studies in the recent twenty years have found some rare-earth-based oxides having higher ionic conductivities to be promising for operation below 600°C, and first-principles simulation studies on the materials have begun.

We studied atomic and electronic properties on oxygen-ionic conduction of $LaGaO_3$-, La_2GeO_5-, Pr_2NiO_4- and CeO_2-based materials by first-principles calculations based on density functional theory (DFT). We analyzed stable structures, electronic densities of states, oxygen migration paths and activation energies in the paths of pure and doped materials in order to evaluate their capabilities in application to electrolytes or electrodes. The obtained results of the activation energies showed good agreements with experiments in several aspects. However, for Pr_2NiO_4- and CeO_2-based materials that contain lanthanoid elements, there remains an open question about theoretical treatment of 4*f* electron states. The strong localization was found to affect oxygen ion motions fundamentally as well as electronic/magnetic properties. Then the strong electron-electron correlation modifies simple trends in activation energies found for the lanthanoid series within an approximation in which the correlation effects were neglected [1].

While fundamental reproduction of the strong electron-electron correlation in localized states by DFT is extremely difficult, empirical corrections by Hubbard *U* terms enable a practical solution to this problem. Here, the *U* value can be determined only by comparison with experiments in most cases because the value is affected by environment of the lanthanoid atoms. However, a theoretical study based on an empirical model demonstrated that the environment effects on 4*f* orbitals can be small if its strong localization is maintained [2]. In the presentation, we confirm this rule based on the results by the DFT first-principles calculations with Hubbard *U* corrections and discuss possibilities of computational materials design of lanthanoid-doped ceria ($Ce_{1-x}Ln_xO_{2-x/2}$) as electrolyte materials.

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4:20pm **AC+AS+MI+SA+SS-MoA8 Electronic Structure, Magnetic Properties, and Magneto-Structural Transformations of Rare Earth Magneto-Caloric Materials**, ***Durga Paudyal***, Ames Laboratory, *V.K. Pecharsky, K.A. Gschneidner, Jr.*, Ames Laboratory and Iowa State University **INVITED**

We present first principles modeling of structural and magnetic properties of Gd_5Ge_4 based magneto-caloric materials. The total energy as a function of the shear displacement of slabs confirms stability of experimentally observed crystal and magnetic structures. Small substitutions of the Gd by Y and Lu lead to a catastrophic loss of ferromagnetism, but the substitutions by La have no effect on the magnetism. Furthermore, substitutions of the Ge by Si exert chemical pressure and transform the antiferromagnetic O(II) to the ferromagnetic O(I) ground state. In addition, we present a pathway for estimating the magnetic entropy change in the room temperature giant magnetocaloric compounds, i.e. $Gd_5Si_2Ge_2$, by coupling first principles outputs with the established magneto-thermodynamic models. The theoretical values of the magnetic entropy change compare well with experimental results.

This work was supported by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences, Materials Science and Engineering Division. The research was performed at the Ames Laboratory, which is operated for the U.S. DOE by Iowa State University under contract # DE-AC02-07CH11358.

Applied Surface Science
Room: 316 - Session AS+BI+MC+SS-MoA

The Liquid Interface & Depth Profiling and Sputtering with Cluster Ion Beams
Moderator: Ian Gilmore, National Physical Laboratory, Michaeleen Pacholski, The Dow Chemical Company

2:00pm **AS+BI+MC+SS-MoA1 Quantifying the Impact of Curvature, Convection and Complexity on Dynamic Interfacial Tension of Fluid-fluid Interfaces**, ***Lynn Walker***, Carnegie Mellon University **INVITED**

The ability to control and predict the adsorption of species at fluid-fluid interfaces is a central issue in many materials processing problems. In most processing steps, this adsorption is dynamic and part of a larger transport problem that requires understanding of local fluid flow, bulk diffusion, interfacial curvature and the details of the adsorption and desorption kinetics. We have been developing tools and a protocol to allow the details of transport of surface active species to interfaces to be quantified. Several examples of the characterization of complex fluid-fluid interfaces will be discussed. The dynamics of adsorption of single and multicomponent surfactant mixtures at oil-water and air-water interfaces has been characterized using a microtensiometer. The use of microscale interfaces allows the transport processes involved in adsorption to be analyzed and both diffusion and kinetic parameters characterized. Microscale interfaces with high curvature allow the impact of curvature to be characterized on the dynamic interfacial tension (IFT) and mechanics of the interface. The scale of the device allows the bulk solution in contact with the interface to be changed rapidly. We are able to remove the bulk surfactant at different points in during the dynamics of adsorption by rinsing the interface and continuously replacing the bulk fluid with surfactant-free aqueous phase to investigate the reversibility of adsorption. For a bulky nonionic surfactant, a critical interfacial tension arises that links the transport dynamics to the onset of partial reversibility in the system. By measuring the mechanical properties of pre-rinsed and rinsed interfaces, we also find a critical interfacial tension that leads changes in the elasticity of the interfaces. The impact of changes in interfacial coverage on coalescence and competitive adsorption are characterized to demonstrate the connection between structure of complex interfaces and interfacial behavior.

2:40pm **AS+BI+MC+SS-MoA3 *In Situ* Probing of Liquid Surfaces and Interfaces by Time-of-Flight Secondary Ion Mass Spectrometry**, ***Xiao-Ying Yu***, Pacific Northwest National Laboratory

The surfaces of aqueous phases and films can 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 to enable direct observation of liquid surfaces and liquid-solid interactions. The unique aspect of our approach is that 1) the detection window is an aperture of 2-3 micrometers in diameter, which allows direct imaging of the liquid surface, and 2) surface tension is used to hold the liquid within the aperture. The microfluidic reactor is composed of a silicon nitride (SiN) membrane and polydimethylsiloxane (PDMS) . Its application in time-of-flight secondary ion mass spectrometry (ToF-SIMS) as an analytical tool was evaluated using a variety of aqueous solutions and complex liquid mixtures, some of which contain nanoparticles. Most recently, we demonstrated *in situ* probing of the electrode-electrolyte solution interface (or solid-electrolyte interface, SEI) using a new electrochemical probe based on our original invention. It provides the first direct observation of the surface and diffused layer of SEI in a liquid with chemical speciation using ToF-SIMS. Moreover, we extended the microfluidic reactor for biofilm growth and mammalian cell cultures and real-time correlative characterization by more than one spectroscopy and microscopy technique. Results from our latest development will also be presented in additional to published ones, showcasing new directions and applications using this novel approach based on microfluidics and combined vacuum and ambient spectroscopy and microscopy multimodal imaging.

3:00pm **AS+BI+MC+SS-MoA4 Mass Spectrometric Characterization of Droplet Surfaces at Ambient Pressure**, ***Kaveh Jorabchi***, Georgetown University

Mass spectrometric methods provide excellent selectivity and sensitivity for chemical characterization of samples. For these methods, ionization constitutes a key step where chemical information from the sample is encoded into populations of gas-phase ions. Investigations on electrospray ionization have shown that the ionization efficiency has a positive bias with respect to surface affinity of analytes in droplets, opening a new avenue for liquid surface analysis. This ionization bias stems from higher ion production rates for surface active analytes. To this end, we have developed a new method to monitor gas-phase ion formation rates from charged nano-droplets. A pulsed nano-spray is used to emit a cloud of charged nano-droplets within an atmospheric-pressure mobility cell. The droplets are guided by a pulsed electric field through the mobility cell, undergoing desolvation and ion production prior to detection by a time-of-flight mass spectrometer. Each chemical species within the droplets creates an ion cloud. The arrival times of the ions at the mass spectrometer are recorded by varying the on-time of the pulsed electric field within the mobility cell, enabling ion cloud size measurements. We demonstrate that the ion cloud sizes are correlated with ion production rates, reflecting interfacial propensity of the analytes. These measurements are consistent with the ion evaporation mechanism from charged nano-droplets, providing a method for liquid surface analysis based on gas-phase ion formation rates.

3:40pm **AS+BI+MC+SS-MoA6 Organic Depth Profiling Alchemy: Can We Transmute Data into Meaning?**, ***Alexander Shard***, National Physical Laboratory, UK **INVITED**

Argon cluster sources suitable for depth profiling organic materials have developed rapidly and are now widely available and routinely used to analyse materials ranging from organic electronic devices to biological samples. This fantastic progress allows detailed insight into the chemistry and structure of organic materials with depth resolutions below 10 nm over many micrometres. When combined with 2D surface chemical imaging, detailed 3D reconstructions can be obtained allowing the label-free visualisation of chemical distributions which were previously impossible to obtain. However, because detailed understanding of the processes involved is still developing, it is necessary to view such data with scepticism when a quantitative answer is required. Conversely, the ability to perform nearly damage-free profiles of organic materials allows us to answer fundamental questions about surface analytical methods provided that the sample analysed has a known structure and composition.

The recurring questions in organic depth profiling and 3D imaging relate to the depth scale and the translation of a signal into a concentration, or amount of material. At NPL, we have developed reference materials which are designed to address these questions and in this talk an overview of developments in quantitative organic depth profiling will be provided. The use of XPS is shown to provide accurate compositions, as expected. However, there are some practical issues to be understood involving X-ray and electron damage and sample heating. Additionally, XPS suffers from low sensitivity, specificity and lateral resolution compared to SIMS. Whilst SIMS is fast, specific, sensitive and has high lateral resolution it suffers from the lack of an adequate means of converting data into compositions. Here, reference materials have been constructed which enable the most important effects of the sample on SIMS data to be described. These effects are outlined and include an apparent depth of origin difference for secondary ions, surface transient behaviour and the matrix effect. It is also shown how it is possible to use the matrix effect to assess the nanoscale phase separation of materials.

4:20pm **AS+BI+MC+SS-MoA8 Argon Clusters - A Novel Solution for the Depth Profiling of Metal Alloys and Inorganic Materials**, ***Jonathan Counsell***, *H.L. Brannon, S.J. Coultas, S.J. Hutton, A.J. Roberts, C.J. Blomfield*, Kratos Analytical Limited, UK

Depth profiles are routinely used to gain information regarding elemental concentration and chemical composition of complex heterogeneous materials. Ion bombardment removes successive layers, exposing bulk material. The difference in the chemical composition of the surface relative to the sub-surface or bulk is often significant to the mechanical or electrical performance of the material.

Here we will discuss the use of Argon clusters for depth profiling a range of inorganic and alloyed materials. Traditionally, depth profiling inorganic materials employed Ar^+ as the bombardment ion. Unfortunately, monatomic Ar^+ can cause significant damage to the bulk structure of the material and can preferentially remove lighter and less well bound elements leading to misleading results. Recent studies show Argon cluster ions greatly diminish the effects of preferential sputtering with simple metal oxides such as titania.[1] Here we wish to broaden this application to a wider variety of materials including precious metal/non-precious metal binary alloys for novel electrode surfaces and ternary and quaternary chalcogenides. We show that with gentler ions, where the energy per atom can be as low as 5-40 eV, it is possible to greatly reduce bulk damage and the preferential removal of weakly bound elements in complex materials.[2]

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4:40pm **AS+BI+MC+SS-MoA9 Low Temperature Plasma for Crater Edge Depth Profiling of Crosslinking Organic Multilayers: Comparison with C_{60} and Argon Cluster Sputter Sources**, ***Shin Muramoto***, National Institute of Standards and Technology (NIST), *D. Rading,* ION-TOF GmbH, Germany, *B. Bush, G. Gillen,* National Institute of Standards and Technology (NIST), *D.G. Castner*, University of Washington

A model organic layer system consisting of three 1 nm delta layers of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) separated by three 30 nm layers of tris(8-hydroxyquinolinato)aluminum (Alq3) was used to evaluate the effectiveness of helium low temperature plasma (LTP) etching for the preparation of crater edge surfaces for subsequent compositional depth profile analysis. The quality of the depth profile was determined by comparing the depth resolutions of the BCP delta layers obtained from the plasma-etched craters with those obtained using ToF-SIMS dual-beam depth profiling equipped with C_{60}^{2+} and argon cluster ($Ar_{1000 \text{ to } 2500}$) sputter sources. Using the full width at half maximum (FWHM) of each delta peak, the depth resolutions of the second and third delta layers were measured to be 6.9 nm and 6.0 nm for the plasma-etched crater, respectively, which were very close to the depth resolutions of 6.2 nm and 5.8 nm obtained from the argon cluster depth profile. In comparison, the use of a 1/e decay length to approximate the depth resolution gave results that identified the artifacts caused by ion bombardment in SIMS depth profiling. The 1/e decay length for the trailing edge of each delta were 2.0 nm and 1.8 nm for the plasma-etched crater, respectively, while the argon cluster depth profile gave decay lengths of 3.5 nm and 3.4 nm, owing to the longer tails produced by artifacts and possibly by slower sputter rate through the delta layers. For the C_{60}^{2+} depth profile, the need to rescale the axis as a result of a strong nonlinear sputter rate gave artificially improved depth resolutions, where FWHM of the delta peaks were 5.6 nm and 7.3 nm, respectively, and 1/e decay lengths were 1.7 nm and 2.3 nm, respectively. Although some artifacts such as contaminant deposition remain, low temperature plasma was shown to be a viable option for creating crater edges for compositional depth profiling without artifacts seen in ToF-SIMS depth profiling.

5:00pm **AS+BI+MC+SS-MoA10 Desorption/Ionization induced by Neutral Cluster Impact as a Versatile Tool for the Investigation of Sensitive and Complex Biosamples**, *A. Portz,* Justus Liebig University, Germany, *M. Baur,* University of Applied Sciences, Germany, *C.R. Gebhardt,* Bruker Daltonik GmbH, Germany, ***Michael Durr***, Justus Liebig University, Germany

Desorption and ionization induced by neutral clusters (DINeC) can be employed as a soft and matrix-free method for transferring surface-adsorbed biomolecules into the gas phase. Using neutral clusters with polar constituents such as SO_2, the impacting clusters do not only provide the energy necessary for desorption but also serve as a transient matrix in which the desorbing molecule is dissolved during the desorption process. As a consequence, desorption and ionization of oligopeptides and smaller proteins can proceed at comparably low energies of the impacting clusters and without any fragmentation [1]. Using a combination of DINeC and ion trap mass spectrometry, femtomol sensitivity was achieved for standard oligopeptides such as angiotensin II or bradykinin [2]; good ion-to-neutral ratio was observed [3].

In this contribution, we show that the signal of the intact molecules $(M+H)^+$ is predominant even in the case of phospho- and glycopeptides, and typical fragments were observed only in low abundance. The origin of these fragments was investigated by comparison with ESI measurements of the original solution as well as of samples which have undergone a similar treatment as for the preparation of the DINeC samples. In that way, we could show that fragmentation takes place already during sample preparation and DINeC is suitable to directly measure such changes of the samples.

Samples with a multitude of components as obtained from realistic biotechnological processes such as tryptic digest of proteins were also successfully analyzed. Peptide mass fingerprint analysis was applied for the evaluation of the respective spectra with very good sequence coverage and protein score. When compared to ESI or MALDI, a substantial number of the unique peptides which were identified with DINeC were not detected with the other methods. Notably, even in the presence of a large excess of salt in the original solution clear spectra of the intact biomolecules were detected. The results are correlated to the very properties of the DINeC process. The method was furthermore successfully applied to a variety of different classes of molecules such as lipids, dye molecules, and pesticides.

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5:20pm **AS+BI+MC+SS-MoA11 C$_{60}$ and Argon Gas Cluster Ion Sputter Depth Profiling for Quantitative Inorganic Thin Film Analysis**, ***Saad Alnabulsi***, *G.L. Fisher, S.R. Bryan, J.S. Hammond, J.F. Moulder*, Physical Electronics Inc.

A successful sputter depth profile accurately identifies 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][2].

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 while preserving the stoichiometry and chemical structure below the surface[3] [4].

Currently, there is great interest in establishing the viability of these cluster ion sources as an alternative to monoatomic argon ion beam sources for analyzing inorganic semiconductor and glass films, with anticipated improvement in the quantitative accuracy of inorganic depth profile results [5][6].

The purpose of this study is to present a comparative evaluation of quantitative XPS analysis to demonstrate the benefits and limitations of monatomic argon, C$_{60}$, and argon gas cluster ion beam sputtering for compositional inorganic depth profiling.

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[2] V. Smentkowski. *Prog. in Sur. Sci.* **64**, 1 (2000).

[3] T. Nobuta, T. Ogawa. *J. of Mater. Sci.* **44**, 1800 (2009).

[4] C. M. Mahoney. *Mass Spec. Rev.* **29**, 247 (2010).

[5] Y. Yamamoto, K. Yamamoto. *Mater. Sci. Eng.* **18** (2011).

[6] D. Kobayashi, Y. Yamamoto, T. Isemura. *Sur. and Inter. Anal.* **45** 113 (2013).

Surface Science
Room: 309 - Session SS+EN-MoA

Metals, Alloys and Oxides: Structure, Reactivity & Catalysis
Moderator: Jason Weaver, University of Florida

2:00pm **SS+EN-MoA1 High Throughput Discovery and Optimisation of Metal Alloy Electrocatalysts**, ***Brian Hayden***, University of Southampton **INVITED**

High-throughput synthesis and screening methodologies provide a powerful tool for the optimisation of alloy electrocatalysts. Libraries of thin film metal alloys have been synthesised using MBE sources to produce compositional gradient thin films in masked fields on micro-fabricated electrochemical screening chips. Examples will be given of ternary metal alloy catalysts designed as alternatives to platinum for the oxygen reduction reaction at the cathode in PEM Fuel Cells. The combination of ab-initio theory and high throughput synthesis and electrocatalyst screening is also shown to provide a powerful combination in the search for alternative catalysts to platinum for hydrogen oxidation at the anode. The approach has also been extended to the development of PdCu and PdSn alloys for the electro-reduction of nitrate, alloys which exhibit strong compositional dependencies which can be related to the redox behaviour of the surfaces. A full structural characterisation allows a direct comparison of catalytic activity to not only composition but also to the structure and phase of the alloy. In addition to measuring the total activity of the electrocatalysts, a secondary screen has been developed adapting the Differential Electrochemical Mass Spectroscopy (DEMS) method to assess the specificity of the reaction to produce the desired gas phase product.

2:40pm **SS+EN-MoA3 Methanol Oxidation on Pt-Re Surfaces: Ambient Pressure XPS and Reactor Studies**, *A.S. Duke, R.P. Galhenage, K. Xie,* University of South Carolina, *S.A. Tenney, P. Sutter,* Brookhaven National Laboratory, ***Donna Chen***, University of South Carolina

Methanol oxidation has been investigated on Pt-Re bimetallic surfaces in order to understand how the addition of Re promotes activity on Pt in alcohol reforming and other oxidation reactions. Pt-Re alloy surfaces were prepared by depositing Re on Pt(111) or polycrystalline Pt foils and annealing to 1000 K. Scanning tunneling microscopy studies demonstrate that the deposited Re islands diffuse into the Pt(111) surface upon annealing, and low energy ion scattering studies indicate that the top monolayer consists mainly of Pt. XPS investigations were carried out at the X1A1 beamline at the National Synchrotron Light Source under methanol oxidation conditions of 200 mtorr O$_2$/100 mtorr methanol between 300 and 550 K, and gaseous products were monitored using a mass spectrometer. Methanol oxidation was studied on clean Pt(111), the Pt-Re alloy and Re films grown on Pt before and after surface oxidation at 450 K. The main products on all surfaces were CO$_2$ and H$_2$O with formaldehyde, CO and H$_2$ as minor products. On the unoxidized surfaces, the selectivity toward H$_2$ and CO production increased above 500 K. Deposition of atomic carbon during reaction was suppressed on the Pt-Re alloy surfaces as compared to pure Pt, and the oxidized Pt-Re alloy was found to reach maximum activity at the lowest temperatures. The Re films were unstable under methanol oxidation conditions at temperatures above 450 K due to the sublimation of Re oxides, but the Re in the Pt-Re alloy remained on the surface under the same conditions. Activity studies in a flow reactor coupled to the ultrahigh vacuum chamber showed that methanol oxidation activity increases with surface oxidation; unoxidized Pt and Pt-Re surfaces initially exhibit minimal activity until the surface becomes oxidized under reaction conditions.

3:00pm **SS+EN-MoA4 Ångstrom-resolved Real-Time Dissection of Electrochemically Active Noble-Metal Interfaces during Oxidation and Reduction**, *B.R. Shrestha, T. Baimpos, S. Raman,* ***Markus Valtiner***, Max Planck Institut fur Eisenforschung GmbH, Germany

Electrochemical metal-oxide|liquid interfaces are critically important for a variety of technological applications and materials for energy storage, harvesting and conversion. Yet, a real-time Ångstrom-resolved visualization of dynamic processes at electrified metal-oxide|liquid interfaces has not been feasible. Here we present a unique direct and real-time atomistic experimental view into dynamic processes at electrochemically active metal interfaces using white light interferometry in an electrochemical surface forces apparatus. This method allows to simultaneously decipher both sides of an electrochemical interface - the solution side and the metal side - in real-time under dynamically evolving reactive conditions, which are typically found in technological systems *in operando*. Quantitative *in situ* analysis of the electrochemical oxidation and reduction of noble metal surfaces shows that the Å-thick oxide films formed on Au and Pt are reflecting high-*ik* materials, *i.e.* they are metallic or highly doped semiconductors, while Pd forms a transparent low-*ik* oxide during dynamic change of applied electrochemical potentials. In contrast, under potentiostatic growth conditions all electrochemically grown noble metal oxides are transparent, with thicknesses ranging from 2-10 Å. On the solution side the data simultaneously reveals hitherto unknown strong electrochemical depletion forces, which are due to a temporary charge imbalance in the electric double layer caused by the consumption or generation of charged species. The real time capability of our approach shows significant time lags between electron transfer, oxide reduction/ oxidation and solution side equilibration during a progressing electrode process. Comparing the kinetics of solution side and metal side reactions provide detailed experimental evidence that noble metal oxide reduction initiates via hydrogen loading and subsequently proceeds via a dissolution/

re-deposition mechanism. The presented approach may have important implications for designing emerging materials utilizing electrified interfaces such as fuel cells, batteries or super-capacitors.

3:40pm **SS+EN-MoA6 Catalytic Dehydration of 2-propanol on Size Selected $(WO_3)_n$ and $(MoO_3)_n$ Metal Oxide Clusters**, ***Xin Tang***, Johns Hopkins University, *D. Bumueller, G. Gantefoer,* Universität Konstanz, Germany, *D.H. Fairbrother, K.H. Bowen*, Johns Hopkins University

Metal oxide nanoparticles and clusters are widely used as redox and acid/base catalysts in heterogeneous catalysis. The catalytic activity of the size selected metal oxide clusters $(WO_3)_n$ and $(MoO_3)_n$ (n = 1, 2, 3, 5, 30) were studied as a function of their size. The 2-propanol dehydration reaction was conducted on both two cluster catalysts. Temperature programmed reaction (TPR) was utilized to characterize the catalytic activity of the deposited cluster catalysts. The cluster size, supporting substrates, and the chemical compositions of the clusters were found to play an important role in determining the catalytic activity of the metal oxide clusters. For tungsten oxide clusters on the annealed oxide films, the catalytic activity of the clusters was found to be linear correlated to the size of the cluster. In addition, lower catalytic activity was observed for $(WO_3)_1$ monomer supported on the HOPG surface compared to the annealed oxide support. Meanwhile, molybdenum oxide clusters exhibited low catalytic activity toward 2-propanol dehydration reactions.

4:00pm **SS+EN-MoA7 Growth and Characterization of Ultrathin ZnO Layers on Au(111) – STM Study of Growth Mode and Adsorption of Water**, ***Junseok Lee***, *X. Deng, D.C. Sorescu*, National Energy Technology Laboratory

Zinc oxide is an important material in the low-temperature synthesis of methanol. In this study, the growth mode of ZnO ultrathin films has been studied on the Au(111) surface using scanning tunneling microscopy (STM). The ultrathin ZnO layers have been found to grow by forming islands on Au(111). Different growth conditions during reactive deposition resulted in ZnO islands whose thickness ranging from one to four layers. The STM results and the density functional theory (DFT) calculation have been used to model the observed phenomena. STM results indicate that the brightness of the Moire pattern of the ZnO layer on Au(111) surface is significantly modulated by the adsorption of water molecule at the positive tip bias. Various water adsorption sites have been identified in the STM results after annealing the sample to various temperatures that correspond to temperature programmed desorption (TPD) peaks. The DFT calculation results provide the most stable configurations of water molecules at each adsorption site.

4:20pm **SS+EN-MoA8 *In Situ* Imaging of the Dynamic Interaction of the Oxide with the Atomic Steps During the Oxide Growth on NiAl(100)**, ***Hailang Qin***, SUNY Binghamton, *X. Chen,* Biola University, *P. Sutter,* Brookhaven National Laboratory, *G.W. Zhou*, SUNY Binghamton

Ultrathin oxide films on metal supports represent a unique combination of materials systems with potential applications ranging from heterogeneous catalysis to electronic devices. In particular, the oxidation of NiAl alloys has received extensive interest for its ability to form a well-ordered Al_2O_3 film. Here we study the dynamic interaction of the atomic steps with the oxide stripes during their growth on single-crystal NiAl(100) at high temperature. With in-situ low-energy electron microscopy (LEEM) imaging and theoretical modeling, it is shown that the oxygen surface diffusion is the main mechanism controlling the oxide growth kinetics while the migration and shape evolution of the substrate steps follows the fluid-like Hele-Shaw flow governed by the attachment/detachment of Al atoms at step edges. When the oxide stripe encounters a series of step edges, the step edges are “pushed” along with the oxide stripe growth and bent towards the growth direction of the stripe. However, the growing oxide stripes do not cross over the substrate steps; instead, they stay on the same terrace even after encountering a number of step edges. Such a process is reversible during the oxide decomposition. The scanning tunneling microscopy (STM) images of the oxide stripes and the atomic steps after the interaction further confirm that the oxide stripes stay on the same terrace after encountering multiple substrate steps, instead of crossing the step edges.

4:40pm **SS+EN-MoA9 Subsurface Oxygen on Ni(111) and Ag(111)**, ***Daniel Killelea***, *J. Derouin, R. Farber*, Loyola University Chicago

Subsurface oxygen atoms are enigmatic sources of energetic reagents in the heterogeneously catalyzed partial oxidation of small hydrocarbons on metal surfaces. Subsurface oxygen atoms are absorbed in the selvedge of a metal, and may emerge to the surface at elevated temperatures to react with adsorbed molecules. Furthermore, when subsurface atoms emerge from beneath adsorbed molecules new reaction geometries are enabled that are otherwise inaccessible between reactants co-adsorbed to a surface. Although believed to be important reactive intermediaries, a systematic study of their fundamental chemistry has yet to be undertaken. To address this, we have selected two model systems for study; oxygen on Ni(111) and Ag(111). These are two systems that will provide basic details of subsurface absorption and reactivity, and further provide guidance for utilization of these species to selectively control chemistry. Subsurface atoms are key components of catalytic processes, but it remains unclear how they enhance reactions. The surface-subsurface dynamics will be elucidated using scanning tunneling microscopy (STM) to image the surfaces with and without subsurface O atoms. We will use the images to determine the presence of a bias for particular surfaces sites for the absorption / emergences processes and further study any structural or electronic effects of the subsurface O atoms on the host metal surface. To complement STM images, temperature programmed desorption and Auger electron spectroscopy will identify adsorbates and provide thermodynamic information. Our results will show mechanisms for subsurface migration and we will also probe the energetics of subsurface incorporation. Taken together, this new information seeks to narrow the gap our understanding between model and actual catalytic systems and enable chemists to accurately gauge the role of subsurface species in the transformation of plentiful feedstock into energy-rich chemicals over metal catalysts.

5:00pm **SS+EN-MoA10 Direct Imaging of the Amphiprotic Nature of Rutile (110) Surfaces in Solution**, ***Dapeng Jing***, *A. Song, M.A. Hines*, Cornell University

High-profile applications of nanocrystalline TiO_2, such as next-generation solar cells and self-cleaning surfaces, have triggered extensive studies on the structure and chemical reactivity of rutile surfaces. But are UHV-prepared clean surfaces a good representation of technologically relevant surfaces? In this study, we show that a simple aqueous procedure produces near-ideal hydrocarbon-free rutile (110) surfaces characterized by well-defined terraces and nearly straight, single-layer-high steps without high-temperature annealing. The structure of rutile surfaces after water exposure is very different from that observed on UHV-prepared clean surfaces. In particular, the O vacancies that dominate the reactivity of surfaces in UHV are not present, as evidenced by both XPS spectra and STM images. This water-induced “healing” of O vacancies is consistent with chemical intuition. The step structures, too, are quite different. In addition, the amphiprotic nature of the surface is directly observed in STM. Depending on the *p*H of the solution, a low density of protrusions decorate either the Ti rows or the bridging oxygen atoms, consistent with *p*H dependent protonation/deprotonation of the basic/acidic sites on the surface. No evidence of the corresponding counterions is observed.

5:20pm **SS+EN-MoA11 Water Splitting Kinetics at MgO(100) Terrace Sites**, ***John Newberg***, University of Delaware

Understanding the surface chemistry of water with metal oxide interfaces has important implications in energy and environmental research. In order to understand surface kinetics and thermodynamics under environmental conditions, in situ molecular level studies are needed to assess adsorbate chemistry and coverage under conditions where adsorption and desorption occur concomitantly. In this talk we will outline a proposed precursor kinetic model to describe recently published ambient pressure XPS (APXPS) results for MgO(100) terrace hydroxylation observed under adsorption-desorption conditions. By combining APXPS with computational studies, mechanistic details for water dissociation on MgO(100) terrace sites are put forth.

2D Materials Focus Topic
Room: 310 - Session 2D+AS+BI+PS+SS-TuM

2D Materials: Surface Chemistry, Functionalization, Bio and Sensor Applications
Moderator: Richard Osgood, Columbia University

8:00am **2D+AS+BI+PS+SS-TuM1 Phase Engineering in 2D Transition Metal Dichalcogenides**, ***Manish Chhowalla***, Rutgers University **INVITED**

Two-dimensional transition metal dichalcogenides (2D TMDs) — whose generalized formula is MX_2, where M is a transition metal of groups 4–7 and X is a chalcogen — exhibit versatile chemistry and consist of a family of over 40 compounds that range from complex metals to semiconductors to insulator. Complex metal TMDs assume the 1T phase where the transition metal atom coordination is octahedral. The 2H phase is stable in semiconducting TMDs where the coordination of metal atoms is trigonal prismatic. Unlike mechanical exfoliation and chemical vapor deposition, chemical exfoliation of semiconducting layered TMDs yields monolayered nanosheets with heterogeneous atomic structure consisting of metallic (1T) and semiconducting (2H) phases. Metal (1T phase) to semiconductor (2H phase) transition can be achieved via mild annealing of exfoliated materials. Semiconductor to metal transitions can be achieved via chemistry. The 1T phase in *semiconducting* TMDs has scarcely been studied but it deserves urgent attention as it exhibits promise as a hydrogen evolution catalyst and as contact electrode in electronic devices. We will describe these phase transitions in semiconducting TMDs and provide examples of how we have learned to exploit them for covalent functionalization, enhanced catalytic and electronic performance.

8:40am **2D+AS+BI+PS+SS-TuM3 Transition Metal Nanoparticles on Single-Layer MoS_2: Structural, Electronic and Catalytic Properties**, ***Takat B. Rawal***, *D.T. Le, T.S. Rahman*, University of Central Florida

We will present results of density functional theory based calculations of the geometric and electronic structure of several types of sub-nanometer sized transition metal nanoparticles (TMNPs) on pristine and defect-laden single-layer MoS_2. We will show that among the investigated TMNPs (Cu, Ag, Au), Cu nanoparticles bind strongest to pristine MoS_2 while Au and Ag nanoparticles bind with similar, weaker strengths. The presence of the vacancy defect on MoS_2 enhances significantly the binding strength of Cu nanoparticles, while it has very little effect on the binding strength of Au NPs. More interestingly, the amounts of charge transfer from TMNPs to MoS_2 vary following the order of the bind energies of TMNPs on MoS_2. Additionally, the shape of the nanoparticles also has an impact on the binding characteristics. Of particular interest is the role of the substrate on the catalytic properties of the TMNP and conversely that of the TMNP on the defect-laden MoS_2 single layer. In this regard we will examine in detail the reactivity of the atoms at the TMNP/MoS_2 interface in reactions such as CO oxidation and methanol decomposition and compare them to that of similar nanoparticles when supported on titania.

Work supported in part by DOE Grant No. DE-FG02-07ER15842

9:00am **2D+AS+BI+PS+SS-TuM4 How Fluorination Enhances Friction Forces for Graphene**, ***Xin Liu***, *Q. Li,* University of Pennsylvania*, S.P. Kim,* Brown University*, V.B. Shenoy,* University of Pennsylvania*, P.E. Sheehan, J. Robinson,* Naval Research Laboratory*, R.W. Carpick*, University of Pennsylvania

The chemical functionalization of graphene can alter its electronic, chemical, mechanical, and tribological properties. Here we employ atomic force microscopy (AFM), Raman microscopy, and molecular dynamics (MD) simulations to show that friction can be fine-tuned by chemically modifying graphene. Although bulk fluorinated graphite has a very low surface energy, our experiments and simulations both show that friction between nanoscale tips and FG is up to 9 times higher than that for pristine graphene. The ability to resolve an ordered lattice in atomic stick-slip friction measurements also diminishes with greater fluorination, indicating that the fluorinated graphene is disordered. Our observation suggests that AFM friction measurements provide a sensitive local probe of the degree of fluorination of graphene. Motivated by MD simulations, we propose that the dramatic enhancement of friction results from increased corrugation of the interfacial potential due to the strong local charge concentrated at fluorine sites, consistent with the Prandtl-Tomlinson model.

9:20am **2D+AS+BI+PS+SS-TuM5 Chemical, Structural and Electrical Modification of Graphene**, ***Sandra Hernández***, *E.H. Lock, M. osofsky, S. Tsoi,* Naval Research Laboratory*, C. Junkermeier,* Penn State University*, R. Stine,* Nova Research*, J. Robinson,* Naval Research Laboratory*, A. Nath,* George Mason University*, V.D. Wheeler, R.L. Myers-Ward, J. Caldwell, C.R. Tamanaha, T. Reinecke, P.E. Sheehan, D.K. Gaskill, S.G. Walton*, Naval Research Laboratory

2D nanomaterials have been vigorously investigated due to their superlative mechanical, thermal, and electronic properties. Being composed entirely of surface atoms, they are incredibly amenable to surface modification thus providing the opportunity towards excellent control over their properties. Surface engineering of 2D materials composed of carbon materials, such as graphene, can be achieved by plasma modification. We will discuss our efforts in understanding the chemical, structural, and electrical properties of plasma functionalized graphene by introducing -oxygen, -fluorine, and -nitrogen chemical moities, and discuss their impact on chemical reactivity, electrical transport, and enhanced sensing behavior. Demonstrating how precise nano-engineering of surface chemistry impacts contact engineering, biosensing and device based applications.

This work is supported by the Naval Research Laboratory Base Program.

9:40am **2D+AS+BI+PS+SS-TuM6 The Mechanochemistry of Chemically Modified Graphene**, ***Jonathan Felts***, *S.C. Hernandez, A.J. Oyer, J. Robinson, S.G. Walton, P.E. Sheehan*, Naval Research Laboratory

Defining the optoelectronic properties of graphene through controlled chemical functionalization provides a route to fabricating a wide range of graphene based devices. In prior work, we showed that heat supplied by a scanning probe removed functional groups from chemically modified graphene (CMG) thereby restoring it to graphene [1]. Here we show that mechanical stress alone effectively removes functional groups. We measured the degree of surface functionalization by monitoring both normal load and friction between the sliding tip and a plasma processed CMG sheet. For oxygenated graphene, friction decayed exponentially with sliding distance, dropping to ~15% of the starting value. These measurements revealed an initial drop in friction that was independent of applied stress, suggesting the presence of an adsorbed water layer on the surface. More importantly, they reveal an Arrhenius-like relationship between contact stress and degree of surface reduction. The reduction in friction persisted, precluding the presence of the adsorbed contaminants as the source of the friction change. Conductive AFM and Raman measurements provide further evidence for chemical reduction. Conductive diamond AFM tips measure the current through the surface during the reduction process, revealing a 5x increase in conductivity corresponding to the friction force reduction. Additionally, Raman measurements on a 5 mm^2 reduced area showed a relative increase in both the G and 2D peaks, consistent with a reduction in functionalization. These experiments enabled detailed comparison of tribochemical reactions without the complications of transfer films or the initial run-in of the film. They also enable experiments difficult by other means. For instance we could directly compare the mechanical barrier to functional group removal by monitoring friction while slowly ramping the applied stress between the tip and a graphene surface functionalized with either oxygen or fluorine groups. For oxygenated graphene, the contact stress at the maximum reduction rate was ~0.47 ± 0.14 GPa; for fluorinated graphene it was ~0.85 ± 0.27 GPa. Thus, by using the same tip and same supporting substrate we could directly compare the bond strengths between different functional groups and the graphene lattice. This work demonstrates the ability to measure and control the chemistry of single-layer functionalized surfaces at the nanometer scale, and has wide application in tribochemical wear, mechanochemistry, and nanoelectronic device fabrication with chemically tuned optoelectronic properties.

[1] Z. Wei, et al, *Science* **328**, 1373-1376 (2010)

11:00am **2D+AS+BI+PS+SS-TuM10 Fe-catalyzed Etching of Graphene, Few-Layer Graphene, and Graphite**, ***Guangjun Cheng***, *A.R. Hight Walker*, National Institute of Standards and Technology

Mechanically exfoliating graphite onto a substrate provides a family of layered materials with adjustable thickness, including monolayer graphene, few-layer graphene (FLG), and graphite. In this work, we investigated the Fe-catalyzed etching of graphene, FLG, and graphite in forming gas (10% H_2/90% N_2) or N_2 using low-voltage scanning electron microscopy and Raman spectroscopy. Fe thin films were deposited by sputtering onto mechanically exfoliated graphene, FLG, and graphite flakes on a Si/SiO_2 substrate. When the sample is rapidly annealed in either gas environment, particles are produced due to the dewetting of the Fe thin film and expected to catalyze the etching of graphene, FLG, and graphite. The combined microscopic and spectroscopic evidence reveals a thickness-dependent, catalytic etching behavior in these two gas environments and provides insights into the catalytic mechanisms involving carbon hydrogenation and carbon dissolution.

11:20am **2D+AS+BI+PS+SS-TuM11 Tunable Graphene/Si Schottky Diode Sensor: Before and After Functionalization for Wide Range of Molecular Sensing**, ***MdAhsan Uddin***, *A. Singh, T. Sudarshan, M.V.S. Chandrashekhar, G. Koley*, University of South Carolina

Graphene/Semiconductor Schottky devices attracted significant research attention due to wide range of applications from transistor to IR detector [1-2]. Such heterojunctions are also promising for sensing applications due to the molecular adsorption induced Schottky barrier height (SBH) change at the interface, affecting the junction current exponentially in reverse bias, which leads to ultrahigh sensitivity. Graphene/p-Si diode sensor [Device image, Raman spectra and I-V characteristics shown in fig. 1(a), (b) and (c)] has been developed with high bias-dependent sensitivity and low operating power.

Performance enhancement has been demonstrated by fabricating graphene chemiresistor and diode sensor on the same chip. The diode sensor exhibited 13 times higher sensitivity for NO_2 [Fig. 2(a)] and 3 times higher for NH_3 [Fig. 2(b)] in ambient condition, while consuming ~500 times less power for same applied voltage. Sensing tunability is achieved by operating the device in reverse bias, tuning the graphene work function and hence the SBH by the applied bias. The sensitivity varied from 268 to 574% for NO_2 as the bias magnitude varied from -1 to -8V [Fig. 3(a)]. Optimized sensor design to detect particular analyte is also possible by careful selection of graphene/Si heterojunction SBH. For example, graphene/p-Si with larger SBH is better NO_2 sensor while smaller SBH device has better NH_3 sensitivity. The sensing mechanism based on SBH change has been confirmed by capacitance-voltage measurements [Fig. 3(b)]. The SBH decreased by 0.23eV for NO_2 exposure while increased by 0.16eV for NH_3. Variation in sensitivity with NO_2 and NH_3 concentration has also been demonstrated (Fig. 4).

Pd and Pt functionalization has been carried out to make the graphene/Si diode [Fig 5] sensitive to H_2. Extrapolated SBH from the I-V characteristics, before and after few nm metal decoration, and H_2 exposure showed initial SBH decrease after functionalization and subsequent increase in presence of H_2, respectively [Fig. 6(a) and (b)]. Compared to graphene chemiresistor, the chemi-diode sensor offers more than one order of magnitude higher H_2 sensitivity for both types of functionalization. Similarly, the reverse bias operation also enables low power consumption, tunable sensitivity and detection of H_2 down to 1 ppm [Fig. 7(a)] in air which is close to the atmospheric background of 0.6 ppm [3]. Among the two metals, Pd-functionalization always exhibited better sensing response irrespective of the bias voltage [Fig. 7(b)]. Remarkably, for Pd-functionalization, the sensor response showed absolute exponential change with varying H_2 concentration ranging from 2 to 1000 ppm [Fig. 7(c)].

12:00pm **2D+AS+BI+PS+SS-TuM13 Dielectrics Layer Deposition on Graphene Surface by Functionalization with Polar Titanyl Phthalocyanine**, ***Jun Hong Park***, *I.J. Kwak, K. Sardashti, 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 monolayer low-k dielectric or as a nucleation layer for growth of high-k insulators. This study demonstrates the molecular scale observation of formation of O-TiPc mono and bilayers on graphene with UHV scanning tunneling microscopy (STM). O-TiPc monolayers were deposited on HOPG surfaces by organic molecular beam epitaxy. After deposition, O-TiPc forms a monolayer with only few defects, and the crystal structure of monolayer has four-fold symmetry in a 1.4 x 1.4 nm grid. Observation of bright protrusions on each O-TiPc indicates that each O-TiPc in the monolayer is directed outward to vacuum. STS shows the band gap of the monolayer is 1.7 eV and the band gap of the bilayer is 2.3 eV. The monolayer or bilayer can directly be employed for sub-nanometer insulators on 2D semiconductors at low bias. Multiple cycles of TMA and water were dosed onto O-TiPc/HOPG to investigate nucleation of Al_2O_3 on the O-TiPc layers. The first cycle of TMA was observed to chemisorb on a 1.4 x 1.4 nm grid on the TiOPc monolayer. After exposure O-TiPc monolayer to 5 cycles ALD pulse (tri-methyl-aluminum (TMA)+H_2O), insulating aluminum oxide was deposited uniformly on O-TiPc/HOPG. After formation of Al_2O_3 on O-TiPc/HOPG, the band gap of surface increases from 1.7 eV to 2.7 eV, while the conductance decreased. As shown in XPS spectra, the quality of Al_2O_3 can be improved by post annealing, consisting with transition of chemical states in O 1s peak and Al 2p. The chemical shifts of O and Al indicate that post annealing converts remained the Al-OH to Al_2O_3. Consequently, O-TiPc can not only act as a low-K dielectric but also induce high density ordered nucleation of ALD on central ion of O-TiPc for high-k dielectric growth.

Actinides and Rare Earths Focus Topic
Room: 301 - Session AC+AS+MI+SA+SS-TuM

Synchrotron Radiation and Laboratory Based Investigations of Actinides and Rare Earths
Moderator: David Geeson, AWE

8:00am **AC+AS+MI+SA+SS-TuM1 The Role of the 5f Band and Partial Occupancy in Actinide L3-edge XANES and RXES Measurements**, ***Corwin Booth***, *S.A. Medling, Y. Jiang,* Lawrence Berkeley National Laboratory, *J.G. Tobin,* Lawrence Livermore National Laboratory, *P.H. Tobash, J.N. Mitchell, D.K. Veirs,* Los Alamos National Laboratory, *M.A. Wall, P.G. Allen,* Lawrence Livermore National Laboratory, *J.J. Kas,* University of Washington, *D. Sokaras, D. Nordlund, T.-C. Weng,* SLAC National Accelerator Laboratory, *E.D. Bauer*, Los Alamos National Laboratory **INVITED**

Although actinide (An) L3-edge x-ray absorption near-edge structure (XANES) spectroscopy has been very effective in determining An oxidation states in insulating, ionically-bonded materials, such as in certain coordination compounds and mineral systems, the technique fails in systems featuring more delocalized 5f orbitals, especially in metals. Recently, actinide L3-edge resonant x-ray emission spectroscopy (RXES) has been shown to be an effective alternative. This technique is further demonstrated here using a parametrized partial unoccupied density of states method to quantify both occupancy and delocalization of the 5f orbital in alpha-Pu, delta-Pu, PuCoGa5, PuCoIn5, and PuSb2. These new results, supported by FEFF calculations, highlight the effects of strong correlations on RXES spectra and the technique's ability to differentiate between f-orbital occupation and delocalization. Potential temperature-dependent spectral changes in the hidden order compound URu2Si2 and the superconductor PuCoGa5 will be discussed.

8:40am **AC+AS+MI+SA+SS-TuM3 Actinide Research with Hard Synchrotron Radiation**, ***Roberto Caciuffo***, European Commission, JRC-ITU, Germany **INVITED**

Advanced x-ray synchrotron radiation techniques, addressing spatial and temporal fluctuations of structural and electronic degrees of freedom, hold outstanding scientific promises for the future of actinide research [1]. Indeed, by probing hidden order parameters and elementary electronic excitations with high sensitivity and resolution, element- and edge-specific (resonant and non-resonant) x-ray scattering experiments provide the bricks for building the novel conceptual frameworks necessary to unravel the complexity of actinides. Here, I will present selected results from these experiments and discuss what they tell us.

Whereas resonant x-ray diffraction (RXD) with photon energies tuned to the $M_{4,5}$ absorption edges of actinide ions are used to study the order of electric quadrupole moments in oxides and intermetallics [2-4], resonant x-ray emission spectroscopy (RXES) and non-resonant inelastic X-ray scattering (NIXS) are applied to study the bulk electronic configuration in solids, liquids and gases [5,6]. In particular, the high penetration depth of hard X-rays employed in NIXS enables flexible containment concepts, facilitating investigations of radioactive materials in the liquid phase or under extreme conditions. Finally, inelastic x-ray scattering (IXS) can be used to map phonon dispersion branches with an energy resolution comparable to the one afforded by inelastic neutron scattering, but using crystal samples with sizes orders of magnitude smaller than those required by neutrons.

In the first example, I will show how a combination of diffraction, RXES, and absorption near-edge spectroscopy experiments at high-pressure can be used to study the correlation between polymorphism, mixing of different electronic configurations, and hybridization effects in elemental americium [7]. The potential of RXD in elucidating the nature of "hidden order" will be illustrated by the examples of the low-temperature phases in NpO_2 [8] and URu_2Si_2 [9]. Then, I will present NIXS results interrogating the $O_{4,5}$ absorption edges of uranium and plutonium materials, and results of IXS studies of the vibrational dynamics in $PuCoGa_5$ and NpO_2.

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9:20am **AC+AS+MI+SA+SS-TuM5 Lumps, Bumps and Pyrophoric Powders - Nuclear Waste Viewed in a New Light**, ***Tom Scott***, University of Bristol, UK, *C.A. Stitt, M. Hart,* Diamond Light Source Ltd., UK, *J. MacFarlane, A. Banos, H. Paraskevoulakos, K. Hallam*, University of Bristol, UK **INVITED**

How do you look inside a nuclear waste package without breaking it open? This question is important when the contained corrosion products are potentially flammable and radioactive. Synchrotron x-rays have been used to perform micro-scale in situ observation and characterisation of uranium entrapped in grout; a simulation for some intermediate level waste. Using specially designed analysis cells X-ray tomography and x-ray diffraction have been used to generate both qualitative and quantitative data from a grout encapsulated uranium sample before, and after, deliberately constrained H_2 corrosion. Tomographic reconstructions determined the extent, rates and mechanisms of the oxidation reaction by assessing the relative densities between the materials and the volume of corrosion products. The oxidation of uranium in grout was shown to follow the anoxic U + H_2O oxidation regime, and the pore network within the grout was observed to influence the induction period for the initiation of uranium hydride formation across the surface of the metal. Powder diffraction analysis identified the corrosion products UO_2 and UH_3, and permitted measurement of corrosion induced stress. Together, x-ray tomography and diffraction provide a means of accurately determining the types and degree of uranium corrosion occurring, thereby offering a future means for studying the reactions occurring in real full-scale waste package systems.

11:00am **AC+AS+MI+SA+SS-TuM10 Isotopic Measurements of Uranium in Particles by SIMS**, ***David Simons***, National Institute of Standards and Technology (NIST) **INVITED**

Secondary ion mass spectrometry (SIMS) has become a primary tool for the International Atomic Energy Agency (IAEA) and its Network of Analytical Laboratories (NWAL) to monitor activities at uranium enrichment sites. IAEA inspectors collect samples by wiping surfaces within facilities with cloth wipes that are later distributed to the NWAL for analysis. At the laboratories particles are extracted from the wipes and searched by various means to find those that contain uranium. The uranium-bearing particles are analyzed by mass spectrometry for their isotopic composition that is the key signature to be compared with the declared use of the facility. Large-geometry (LG) SIMS instruments based on magnetic sector mass spectrometers with multicollector array detectors are used by five members of the NWAL to both search for the uranium particles and analyze those that are found. We have characterized the performance of this type of instrument and found that it can be set up with a mass resolving power that excludes nearly all mass spectral interferences from uranium isotopes while maintaining high instrument transmission and high abundance sensitivity. The total efficiency for uranium detection has been measured with monodisperse microspheres and found to exceed 1 %. Detection of U236 presents a special case because of interference from the U235 hydride ion that is removed by peak-stripping. The effect of the hydride on the uncertainty in the U236 abundance determination has been modeled for different uranium enrichments and hydride-to-parent ratios, and the effect of the particle substrate on hydride production has been investigated. The performance of LG-SIMS instruments for isotopic measurements of uranium in particles was recently demonstrated in the NUSIMEP-7 study organized by the Institute of Reference Materials and Measurements in which these instruments were able to detect and measure all uranium isotopes in particles smaller than 400 nm, including U236 at an isotopic abundance of $8x10^{-6}$.

11:40am **AC+AS+MI+SA+SS-TuM12 X-ray Excited Auger Transitions of Pu Compounds**, ***Art Nelson***, *W.K. Grant, J.A. Stanford, W.J. Siekhaus, W. McLean*, Lawrence Livermore National Laboratory

X-ray excited Pu NOO Auger line-shapes were used to characterize differences in the oxidation state of Pu compounds. The Auger line-shapes were combined with the associated chemical shift of the Pu $4f_{7/2}$ photoelectron line, which defines the Auger parameter and results in a reliable method for definitively determining oxidation states independent of binding energy calibration. Results show that PuO_2, Pu_2O_3, $PuH_{2.7}$ and Pu have definitive Auger line-shapes. These data were used to produce a chemical state (Wagner) plot for select plutonium oxides. This Wagner plot allowed us to distinguish between the trivalent hydride and the trivalent oxide, which cannot be differentiated by the Pu $4f_{7/2}$ binding energy alone.

In-Situ Spectroscopy and Microscopy Focus Topic
Room: 313 - Session IS+AS+MC+SS-TuM

Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS)
Moderator: Franklin (Feng) Tao, University of Notre Dame

8:00am **IS+AS+MC+SS-TuM1 The ISISS Facility at BESSY II and Beyond: The Application of Near Ambient Pressure X-ray Electron Spectroscopy in the Surface Characterization of Technical Catalysts**, ***Michael Hävecker***, Helmholtz-Zentrum Berlin für Materialien und Energie/Elektronenspeicherring BESSY II, Germany, *Ch. Heine, M. Eichelbaum,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, *F. Rosowski,* BasCat, UniCat-BASF JointLab, Germany, *A. Trunschke, R. Schlögl*, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany **INVITED**

The surface of functional materials like catalysts responds to the ambient conditions. Surface sensitive in-situ spectroscopy, i.e. in the presence of a reactive gas allows studying the formation of the gas/solid interface of a catalyst. The ISISS facility operated by the FHI at the synchrotron radiation source BESSY II of the HZB is dedicated to this kind of in situ studies [1 - 3]. Online gas analytics allows correlating the electronic surface structure with the catalytic performance. Examples for the dynamic formation of the electronic surface structure by interaction with the ambient gas under equilibrium will be presented focusing on technical catalysts like multi-element mixed oxide powders. The direct catalytic oxidation of alkanes to olefins and oxygenates is becoming increasingly important for the chemical industry due to the up-coming shortage of crude oil resources. Vanadyl pyrophosphate is the industrially used catalyst in the selective oxidation of n-butane to maleic anhydride. We characterized the surface of this catalyst material with NAP-XPS in the mbar pressure range and with NAP-soft XAS in the electron yield mode at pressures up to 1000mbar at various gas mixtures. In addition to the determination of composition and vanadium oxidation state also semiconductor properties like work function changes and Fermi level pinning have been studied [4].

Finally, an outlook on future activities at HZB/BESSY to develop further synchrotron based ambient pressure characterization methodologies will be given. The Energy Materials In-Situ Laboratory Berlin (EMIL) is a research alliance of the HZB and FHI that will include a NAP-high kinetic energy XPS endstation capable to operate at kinetic energy of photoelectrons up to 7000eV that allows studying buried layers and liquid/solid interfaces.

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8:40am **IS+AS+MC+SS-TuM3 Recent Trends and Instrument Development in Ambient Pressure Photoelectron Spectroscopy**, ***Henrik Bergersen***, *J. Åhlund*, VG Scienta AB, Sweden

The field of Ambient Pressure Photoelectron Spectroscopy (APPES) has gone through rapid development in recent years. Although the field was pioneered in the 1970's, most instrument as well as application development has happened in the last decade. In this contribution we will discuss some recent trends in APPES and present state-of-the-art work within the different applications areas.

Experiments done under normal surface science conditions (Ultra High Vacuum) are of limited use in some applications, e.g. catalysis, due to the pressure gap problem. This motivates the study of systems at ambient pressures. While the presence of a gas atmosphere surrounding the sample enables new types of studies, it also poses instrumentation difficulties. The most notable of these is signal decrease due to inelastic scattering of the photoelectrons in the surrounding gas. We will show state-of-the-art solutions to limit this scattering together with recent results.

Photoelectron spectroscopy went through a revolution in the 1990's, with the development of parallel angular detection using 2D detectors, a development that VG Scienta is proud to have contributed to. The possibility of simultaneous recording of Angular Resolved PES (ARPES) spectra enables not only band structure measurements, but also x-ray photoelectron diffraction (XPD), depth profiling and standing wave spectroscopy. Recent examples within APPES will be given.

The use of 2D detectors to record parallel spatially resolved spectra is a related technique. Here we will show experimental results as well as very recent instrument development to obtain world leading spatial resolution at ambient conditions.

The combination of APPES and Hard X-ray Photoelectron Spectroscopy (HAXPES) has recently become an established technique. We will show results of the use of this combination to decrease inelastic scattering of the photoelectrons as well as to tailor the probing depth of advanced systems.

In APPES, more than in UHV PES, instrument usability and sample handling is a key to successful measurements. VG Scienta has developed several complete system offerings to maximize productivity in the lab. These will be discussed on a conceptual level, as well as in some detail.

9:00am **IS+AS+MC+SS-TuM4 *In Situ* Studies of Exceptionally Active Catalyst of Earth Abundant Elements for Complete Combustion of Methane at a Relatively Low Temperature**, *F. Tao, J. Shan, L.T. Nguyen, S. Zhang,* ***Weixin Huang***, University of Notre Dame

It is critical to develop a catalyst made of earth-abundant elements highly active for a complete combustion of CH_4 at a relatively low temperature for catalytically transforming CH_4 to electrical energy in power plant. The currently available catalysts with high activity consist of precious metal nanoparticles supported on rare earth oxides. Their high cost limits the application of these catalysts at industrial scale. Here we report a new catalyst, early transition metal oxide-based mixed oxide only consisting of earth-abundant elements which can completely combust CH_4 at 350°C at a gas hourly space velocity of 240,000 ml 0.5% CH_4 on 1 gram in one hour. This comparable or even higher catalytic activity results from the integration of Ni cations and surface lattice oxygen atoms at the atomic scale. With such an integration, the carbon atom dissociated from CH_4 can bond with its neighboring surface oxygen atoms to form an intermediate of CO_2 and then desorb.

In-situ studies of catalyst surface using AP-XPS and monitoring of products formed from isotope-labeled catalysts show that (1) molecules O_2 dissociates on surface oxygen vacancies, (2) half of the dissociated oxygen atoms stay in oxygen vacancies, (3) the other half of dissociated oxygen atoms directly bond with hydrogen atoms dissociated from CH_4 to from OH and then H_2O molecules, (4) CH_4 progressively dissociates on Ni cations to form CH_n (n=3, 2, 1, 0), (5) carbon atoms bind to two surface lattice oxygen atoms nearby to form a carboxylate species, O-C-O intermediate, and then desorb. The mixed cations and surface lattice oxygen atoms in this mixed oxide at atomic level makes the formation of an –O-C-O- intermediate at a mild temperature since a spillover of dissociated species is not necessary.

9:20am **IS+AS+MC+SS-TuM5 Ambient Pressure XPS Studies of Fuel Cell and Electrolysis Catalysis**, ***Hirohito Ogasawara***, SLAC National Accelerator Laboratory **INVITED**

Fuel cell and electrochemical reactions were studied by ambient pressure X-ray photoemission spectroscopy at Stanford Synchrotron Radiation Lightsource (SSRL) [1]. We will present our recent studies: platinum catalyst under different operating conditions of oxygen reduction fuel cell reaction, iridium oxide catalyst during the oxygen evolution reaction and molybdenum sulfides catalyst during the hydrogen evolution reaction. Surface changes under these electrochemical reactions, which are keys to understanding activity and durability will be shown [2,3].

[1] Ambient-pressure photoelectron spectroscopy for heterogeneous catalysis and electrochemistry, CatalysisToday 205 (2013) 101.

[2] Direct observation of the oxygenated species during oxygen reduction on a platinum fuel cell cathode, Nature Communications 4 (2014) 2817

[3] In situ observation of surface species on iridium oxide nanoparticles during the oxygen evolution reaction, submitted

11:00am **IS+AS+MC+SS-TuM10 Environmental Cells with 2D Electron Transparent Windows for Ambient Pressure Photoelectron Imaging and Spectroscopy**, ***Andrei Kolmakov***, National Institute of Standards and Technology (NIST)

We have designed and characterized electron transparent windows for environmental cells dedicated for ambient pressure XPS spectroscopy and electron microscopy of liquid and gaseous samples. These windows made of single or multi-layered graphene have thicknesses comparable to the effective attenuation length of 200-1000 eV electrons what allow to conduct interfacial spectroscopy of fully hydrated samples without differential pumping setup. In addition, these membranes are thermally and chemically stable, gas impermeable and mechanically robust. Based on this unique combination of properties and on recent developments in graphene fabrication and transfer protocols we demonstrate the capability to perform in situ XPS and electron microscopy studies of the electrochemical processes taking place at liquid electrolyte-solid interface.

11:20am **IS+AS+MC+SS-TuM11 The Effect of Interfacial Ethanol on Ionic Distributions in Aqueous Solution**, ***Marijke Van Spyk***, *K.A. Perrine, M.J. Makowski,* University of California Irvine, *H. Bluhm,* Lawrence Berkeley National Laboratory, *J.C. Hemminger*, University of California Irvine

In this study, liquid microjet X-ray photoelectron spectroscopy (LJ-XPS), carried out at beam line 11.0.2 of the ALS synchrotron at LBNL, was used to probe the interfacial behavior of aqueous magnesium or sodium chloride solutions with the addition of organics including ethanol under one torr of water vapor. Our results address fundamental issues of solvation at the surface and in the bulk of ternary solutions. For these studies, aqueous ethanol solutions were generated, and salt was added to produce an ionic solution. The ternary solution is pumped continuously through a temperature-controlled quartz capillary to produce a micron-sized laminar jet within 0.5 mm of the PES analyzer aperture. Synchrotron radiation ionizes the solution, and ejected photoelectrons are detected using differentially pumped electron optics. Tunable photon energy, together with the inelastic scattering attenuation of photoelectrons in solution, provide a variable probe depth. Here, photoelectrons with low kinetic energies (200 eV) are detected from the surface of solution, and those with high kinetic energies (600 eV) are detected from deeper into solution, where chemistry is consistent with bulk solution. The high kinetic energy photoelectrons have sufficiently large inelastic mean free paths so that a percentage are not attenuated by inelastic scattering.

Carbon (C1s), oxygen (O1s), sodium (Na2s), magnesium (Mg2s), and chloride (Cl2p) photoelectron spectra were collected at two photoelectron kinetic energies to investigate the relative concentration of species at the surface and in the bulk for various ethanol concentrations. The C1s spectra were deconvolved into two gas phase and two solution phase peaks corresponding to the carbon groups in ethanol. Surface adsorption was evident for aqueous ethanol without ions, and was diminished in the presence of ions. The relative ionic propensities at the surface change with ethanol concentration. In particular, the solvation of magnesium was impacted by dehydration. Understanding the interfacial solute distribution of these ternary solutions is important for predicting reactivity at aqueous surfaces.

11:40am **IS+AS+MC+SS-TuM12 Studying Zeolites and Clays with the Tools of Surface Science from UHV to Near-Ambient Pressures**, ***Jorge Boscoboinik***, Brookhaven National Laboratory **INVITED**

While Surface Science provided useful insights into a variety of materials of interest for catalysis, its contribution to the understanding of zeolites and clays has been limited. This was mainly due to the lack of suitable well-defined surfaces that successfully mimic the properties of these important materials while allowing its analysis using the vast toolkit of surface science. This talk will describe an aluminosilicate ultra-thin (~ 0.5 nm) film that was recently synthesized, which provides a good model system for zeolites and clays. It consists of a bilayer structure, as shown in the figure, and it counts with bridging hydroxyl groups. The latter are the active sites in zeolite catalysts, of great importance for energy transformations such as the cracking of crude oil and the methanol to gasoline conversion. This model system allows then to study the interaction of molecules involved in these catalytic processes and potentially contribute to the understanding of these chemical transformations. I will provide first a description of the system itself as characterized in ultra-high vacuum (UHV) conditions and then move on to analyze the interaction of these aluminosilicate films with different molecules of interest from UHV to near-ambient pressures.

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Surface Science
Room: 309 - Session SS+AS+EN-TuM

Synthesis, Structure and Characterization of Oxides
Moderator: Andrew Gellman, Carnegie Mellon University

8:00am **SS+AS+EN-TuM1 Coexisting Accessible Surface Phases on $BaTiO_3$ (001)**, ***Erie Morales***, *J.M. Martirez,* University of Pennsylvania, *W.A. Saidi,* University of Pittsburgh, *A.M. Rappe, D.A. Bonnell*, University of Pennsylvania

Novel ferroelectric $BaTiO_3$ applications ranging from sensors to nanogerators require a detailed understanding of atomic interactions at surfaces. Single crystals provides a platform that allows the explotation of surface physical and chemical properties that can be readily transferred to other ABO_3 perovskite structures. The processes that result in the atomic and electronic structures of surfaces in tandem with details of surface reactivity are necessary steps towards an understanding of $BaTiO_3$. Here we demonstrate that two surface reconstruction phases can coexist on a surface and explain the stability of the surface with a quantitative comparison of thermodynamic and kinetic considerations. Specifically, scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) of atomically resolved c(2x2) and c(4x4) reconstructions on $BaTiO_3$ (100) are compared with density functional theory models to determine the structures of the phases. First principles calculations are also used to examine the thermodynamic stability of the phases and the reaction pathways to both the stable and meta stable structures. We also show the atomic structures of 1 D interfaces between the phases. The ferroelectric properties of $BaTiO_3$ lead to polarization dependent surface reactions and recent results based on poling at atomic level and will be discussed.

8:20am **SS+AS+EN-TuM2 Oxidation and Chemical Reactivity of TbO_x Thin Films on Pt(111)**, *W. Cartas, R. Rai, A. Sathe,* University of Florida, *A. Schaefer,* University of Bremen, Germany, ***Jason Weaver***, University of Florida

Rare earth oxides (REOs) exhibit favorable catalytic performance for a diverse set of chemical transformations, including both partial and complete oxidation reactions. In this talk, I will discuss our recent investigations of the growth, oxidation and chemical reactivity of TbO_x(111) thin films on Pt(111), and make comparisons with results for Sm_2O_3(111) films grown on the same substrate. Bulk terbia and samaria represent examples of REOs that are reducible vs. effectively irreducible, respectively. From low energy electron diffraction and scanning tunneling microscopy, we find that samaria and terbia grow as high quality thin films on Pt(111) during deposition in ultrahigh vacuum. Both oxides develop in the Ln_2O_3 stoichiometry and adopt an oxygen-deficient fluorite structure wherein the metal cations form a hexagonal lattice in registry with the Pt(111) substrate, while oxygen vacancies are randomly distributed within the films. We find that plasma-generated O-atom beams are highly effective in transforming the Tb_2O_3(111) films to higher Tb oxides. Based on results of X-ray photoelectron spectroscopy and O_2 temperature programmed desorption (TPD), we show that exposure to O-atom beams completely oxidizes the Tb_2O_3(111) films to TbO_2 at 300 K, for film thicknesses up to at least seven layers. Heating to ~1000 K in UHV restores the films to the Tb_2O_3(111) stoichiometry, and produces O_2 desorption in two distinct TPD features centered at ~370 K and 660 K which we attribute to oxygen release from lattice sites located in the surface vs. bulk layers, respectively. We also find that O-atom adsorption at 90 K produces a weakly-bound state of oxygen on the TbO_x films which desorbs between ~100 and 270 K. This state of oxygen may correspond to a form of chemisorbed oxygen on the TbO_x film. Consistent with this interpretation, TPD experiments performed after oxidizing a $Tb_2{}^{18}O_3$ film with ^{16}O-atoms demonstrate that oxygen desorption below about 500 K originates only from the oxygen that is “added” to the Tb_2O_3 film, while all isotopic combinations of O_2 desorb from the bulk above 500 K. Lastly, I will present results which show that the oxidized TbO_x films exhibit high activity and selectivity for the dehydrogenation of methanol to formaldehyde, whereas the initial Tb_2O_3 films have limited reactivity toward methanol.

8:40am **SS+AS+EN-TuM3 Structure/Function Relationships on Cerium Oxide: Reactions on Single Crystal Films and Shape-Selected Nanocrystals**, ***David Mullins***, Oak Ridge National Laboratory **INVITED**

Cerium oxide is a principal component in many heterogeneous catalytic processes. One of its key characteristics is the ability to provide or remove oxygen in chemical reactions. Recent work has demonstrated how the reactivity and selectivity of various molecules are dramatically altered on different crystallographic faces of cerium oxide. The structure and composition of different faces determine the number of coordination vacancies (CV) surrounding surface atoms, the availability of adsorption sites, the spacing between adsorption sites and the ability to remove O from the surface. The Ce cation sites are less accessible and have fewer coordination vacancies (CV) on CeO_2(111) than on CeO_2(100). Even though the Ce is in the second layer on CeO_2(100), molecules can adsorb in the open bridge sites between two Ce cations. While there have been numerous studies of the adsorption and reaction of various molecules on CeO_2(111) only recently have comparable experiments been conducted on CeO_2(100).

To investigate the role of surface orientation on reactivity, CeO_2 films with different orientations were grown by two different methods. CeO_2(100) films were grown ex situ by pulsed laser deposition on Nb-doped $SrTiO_3$(100). CeO_2(111) films were grown in situ by thermal deposition of Ce metal onto Ru(0001) in an oxygen atmosphere. The chemical reactivity was characterized by the adsorption and decomposition of various molecules such as CO_2, H_2O, alcohols, aldehydes and organic acids. In general the CeO_2(100) surface was found to be more active, i.e. molecules adsorbed more readily and reacted to form new products, especially on a fully oxidized substrate. However the CeO_2(100) surface was less selective with a greater propensity to produce CO, CO_2 and water as products. Experiments are underway to determine if CeO_2(110), where the Ce adsorption sites are in the top layer and have 2 CV but the O has only 1 CV, will produce an active yet more selective catalyst.

It is possible to synthesize high surface area shape-selected nanoparticles (octahedra and cubes), i.e. powders that expose a single, well-defined surface. Experiments have shown similarities between the single crystal surfaces and shape-selected nanoparticles, e.g. CeO_2(111)/octahedra are less active than CeO_2(100)/cubes. However there have also been significant differences in selectivity and the types of products formed. Possible explanations for the differences on the single crystal surfaces vs. the nanoshapes will be considered.

Research sponsored by the US Department of Energy, Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division.

9:20am **SS+AS+EN-TuM5 Ceria on Cu(110): Formation of Nanostripe Strain Defects**, *L. Ma, N. Doudin, S. Surnev,* ***Falko Netzer***, Karl-Franzens University, Austria

The growth morphology and atomic geometry of ceria nanostructures on Cu(110) have been investigated by STM, LEED and XPS. Ceria grows epitaxially in a two-dimensional (2-D) hexagonal layer, which is associated with a CeO_2(111)-type trilayer structure forming a (3x11) coincidence lattice. An important experimental parameter is the oxygen pressure during growth: it influences the stoichiometry of the ceria overlayer as well as the Cu surface oxide phase, which coexists with the ceria for coverages below the full monolayer. For oxygen pressures in excess of 10^{-7} mbar, stoichiometric CeO_2 and coexisting Cu-c(6x2) surface oxide are formed, whereas for lower oxygen pressures, in the 10^{-8} mbar range, slightly substoichiometric ceria ($CeO_{\sim 1.9}$) and a Cu-(2x1) surface oxide are observed. The ceria overlayer grows essentially 2-D, but displays a peculiar nanostripe pattern, with varying periodicities ranging from 4-8 nm and a corrugation amplitude of 0.2-0.3 nm. This nanostripe pattern is due to a topographic modulation of the overlayer caused by the frustration of overlayer-substrate bonding as a result of the epitaxial mismatch at the ceria-Cu interface. Detailed STM investigation reveals a distortion of the ceria lattice in the transition region between dark (low) and bright (high) stripes, which gives rise to periodic regions of anisotropic lattice strain - socalled "lattice strain defects". It is speculated that these lattice strain defects may support particular chemical reactivity.

Work supported by the ERC Advanced Grant "SEPON" and by the COST Action CM1104

9:40am **SS+AS+EN-TuM6 Design Rules for Stabilizing Polar Metal Oxide Surfaces: Adsorption of O_2 on Zn-rich Polar ZnO(0001)**, ***Ming Li***, *P. Gorai, E. Ertekin, E.G. Seebauer*, University of Illinois at Urbana-Champaign

For oxide semiconductors with appreciable ionic character, under-coordination of the surface atoms leads to thermodynamic instability that is typically restored by reconstruction, faceting, or extensive surface defect creation. Developing design rules for stabilizing polar metal oxide surfaces that avoid these phenomena could offer novel protocols for applications such as improved nanostructure growth and design of photocatalytic heterostructures. The present work describes calculations by density functional theory for Zn-rich polar ZnO(0001) which demonstrate that stabilization via chemisorbed O_2 together with vacancy formation is energetically as favorable as stabilization by vacancies alone. The stabilization mechanism including adsorption is so effective that it promotes O_2 adsorption to an extent that is not possible on non-polar ZnO. Experimental evidence for such stabilization behavior is presented based on measurements of O_2 adsorption on polar ZnO(0001) via the optical modulation technique of photoreflectance. The measured isotherms yield a sizable adsorption enthalpy of adsorption near 1.8eV, confirming a strong interaction with the polar surface.

11:00am **SS+AS+EN-TuM10 The Growth of Catalytic Thin Films on a Polar Substrate: Cr_2O_3 on ZnO (0001) and ZnO (000-1)**, ***Xiaodong Zhu***, Yale University

Zinc oxide is a wurtzite-structured polar crystal with dramatic polarization direction-dependent surface chemistry. Meanwhile, chromium III oxide is a non-polar material catalytically active for a number of industrial chemical reactions, most notably dehydrogenation. Therefore, the Cr_2O_3/ZnO system has been chosen to demonstrate how the polarization direction of a substrate can be exploited tailor the surface properties of catalytically active non-polar thin films. Photoelectron spectroscopy and electron diffraction have been performed to determine the growth mode as well as the film quality. The growth is 2D; however, the films appear initially disordered on both positive and negatively poled substrates. On both substrates the order was observed to improve with thickness. Small band offsets between Cr_2O_3 and oppositely poled substrates were observed that were consistent with charge compensation at the Cr_2O_3/ZnO interface. No obvious change in the oxidation state of the chromium was seen and so it is assumed that the charge compensation at the interface only involves Zn and/or O. The offset between the Cr peaks on positively and negatively poled substrates was obvious at the initial growth stages but then decayed with film thickness, suggesting that the compensating charges at the interface may migrate to the film surface. Valence band spectra were analyzed to characterize the bonding at the interface. The surface chemical behavior of Cr_2O_3 on the two zinc oxide surfaces is being characterized to determine how significantly the polar interface impacts the surface properties of thin supported layers.

11:40am **SS+AS+EN-TuM12 Chemical Characterization of Elements in Oxides using X-ray Satellite Lines**, ***Terrence Jach***, National Institute of Standards and Technology (NIST)

X-ray satellite lines come about in x-ray fluorescence spectroscopy as a result of shake-off events in the excitation process. The ratio of their intensities has been shown to be a sensitive function of their oxidation states. We are able to observe the K satellite lines in the x-ray spectra of oxides and glasses, excited by the beam of an electron microscope and detected by a high resolution x-ray microcalorimeter detector. The results show surprising departures from the expected states of some metal elements that we expect to be fully oxidized. The satellite ratio is a way of determining the chemical environment of insulators without charging or ultra-high vacuum.

12:00pm **SS+AS+EN-TuM13 *In Situ* XPS and NRA Studies of Hydrogen Diffusion in TiO_2 Single Crystals**, ***Vaithiyalingam Shutthanandan***, *M.I. Nandasiri, S.A. Thevuthasan, M.A. Henderson, S. Manandhar*, Pacific Northwest National Laboratory

The intrinsic point defects associated with oxygen vacancies and Ti^{3+} ions play a crucial role in the usage of titanium dioxide (TiO_2) in various technological applications including catalysis and photochemistry. It is well known that the interactions between H atoms and surface oxygen in TiO_2 lead to the formation of Ti^{3+} ions at elevated temperatures. However the Ti^{3+} ion formation and accumulation as a function of elevated temperatures in UHV conditions during hydrogen diffusion in TiO_2 is not well understood. In this study, we have used ion implantation method to incorporate hydrogen in single crystal TiO_2 (110) samples and investigated the behavior of point defects in both pure and hydrogen implanted TiO_2 as a function elevated temperatures using Rutherford backscattering spectrometry (RBS), nuclear reaction analysis (NRA), x-ray photoelectron spectroscopy (XPS) and ultra violet photoemission spectroscopy (UPS). TiO_2 single crystals were implanted with 40 keV hydrogen ions at room temperature with ion fluences of $1x10^{15}$, $1x10^{15}$ and $1x10^{17}$ atoms/cm^2. Samples were isochronally annealed in vacuum for 30 minutes at each temperature up to 1100K and hydrogen and Ti^{3+} defects were quantified. Hydrogen depth profile measurements obtained from $1x10^{17}$ atoms/cm^2 implanted sample reveal that hydrogen diffused towards the surface at lower temperatures and it slowly diffuses out from the samples at higher temperatures. XPS and UPS measurements from the hydrogen implanted samples show significantly higher Ti^{3+} defects in comparison to pure TiO_2 at these temperatures under UHV conditions. These defects reach a maximum around 880 K in which almost all hydrogen was removed from the sample. When the implanted sample further annealed to high temperatures, the amount of Ti^{3+} in hydrogen implanted samples started to decrease and reaches the values from the pure TiO_2 samples around 1100K.

2D Materials Focus Topic
Room: 310 - Session 2D+AS+HI+MC+NS+PS+SP+SS-TuA

2D Materials Characterization including Microscopy and Spectroscopy
Moderator: Manish Chhowalla, Rutgers University

2:20pm **2D+AS+HI+MC+NS+PS+SP+SS-TuA1 Layer-Dependent Electronic and Physical Structure of 2D van der Waals Crystals**, ***Richard Osgood***, Columbia University **INVITED**

Because of their weak Van der Waals interlayer bonding transition-metal dichalcogenide (TMDC) semiconductors can be fabricated into atomically thin two-dimensional (2D) crystals with substantial ~ 1-2 eV bandgaps. As one example, monolayer MoS_2 consists of a single layer of Mo atoms sandwiched between two layers of S atoms in a trigonal prismatic structure. The TMDC 2D system has attracted great interest because of its distinctive electronic and optical properties, such as (i) a transition from indirect-to-direct band gap in going from the multilayer to monolayer crystal due to a missing interlayer interaction in monolayer form and (ii) strong spin-orbit-coupling-induced split valence bands, i.e. 100's of meV, due to broken inversion symmetry, which makes TMDCs interesting for spin-physics physics and devices. Both properties have been predicted with density functional theory (DFT) calculations and indirectly demonstrated using photoluminescence and Raman spectroscopy.

Recently we have made a series of direct observations of the thickness-dependent electronic-band and crystal structure of TMDCs of both exfoliated and CVD grown sample. Because of the relatively modest sample sizes we have used micrometer-scale, angle-resolved photo-emission spectroscopy (micro-ARPES) of both the exfoliated and chemical-vapor-deposition-grown crystals; these measurements provide direct evidence for the shifting of the valence band maximum from gamma bar (Brillouin zone center) to kappa bar (Brillouin zone corner), as the sample thickness decreases from bulk to monolayer. Our initial results were with MoS_2 and are described in a preliminary way in Refs 1 and 2. Our TMDC experimental results are compared with rigorous DFT calculations of both the bands and the UV transitions matrix elements. The results show an evolution in band structure, which is consistent with an indirect-to-direct bandgap transition in going from few-layer to monolayer TMDC and can be attributed to changes in quantum confinement as the number of layer decreases. Our microARPES and, subsequently, higher resolution nanospectroscopy data provide clear measurements of the hole effective mass, the strain present in the monolayer crystal films, and the valence-band spin-orbit splitting. Our results explain the low hole mobility of monolayer MoS_2 compared to thicker MoS_2 and show clearly the strong orbit split energies. Our results, using nanoLEED and LEEM also provide insight into the structure and defects in monolayer films. Experiments using K-doping of single-crystal samples and resulting level shifts are also described.

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3:00pm **2D+AS+HI+MC+NS+PS+SP+SS-TuA3 X-ray Photoemission and Electron Energy Loss Spectroscopy Investigation of the Band Gap and Band Alignment for h-BN and MoS_2 Materials and Interfaces**, ***Benjamin French***, *J. Brockman, M. French, M. Kuhn, J.D. Bielefeld, S.W. King,* Intel Corporation*, E. Bersch, G. Bersuker,* SEMATECH*, J. DiStefano, Y.C. Lin, J.A. Robinson*, Penn State University

Hexagonal boron nitride (h-BN) and molybdenum disulfide (MoS_2) are two dimensional (2D) materials of significant interest for future nano-electronic devices. Due to a wide band gap (~ 6 eV), close lattice matching (< 2%) and atomic planarity, hexagonal boron nitride (h-BN) is of primary interest as a potential substrate and gate dielectric in graphene channel transistor devices. In contrast, MoS_2 is a 2D semiconducting material with a band gap of ~ 1.8 eV that is attractive as a possible complement or alternative to graphene for nano-electronic devices requiring a large band gap. A key property for the success of both h-BN and MoS_2 in such devices is the interfacial band alignment with graphene, the gate contact metallization and the surrounding insulating dielectric materials. In this regard, we have utilized x-ray photoelectron spectroscopy (XPS) to determine the Schottky barrier and valence band offsets present at the interfaces between plasma enhanced chemically vapor deposited amorphous h-BN:H and chemically vapor deposited MoS_2. In combination, we have utilized reflection electron energy loss spectroscopy (REELS) to investigate the band gap of both h-BN and MoS_2 materials to deduce the conduction band alignment. We show that in many instances the valence and conduction band offsets are significant and favorable for MoS_2/h-BN transistor devices.

3:20pm **2D+AS+HI+MC+NS+PS+SP+SS-TuA4 STM/STS Characterization of MoS_2 Monolayers and Nanostructures**, *A. Mills, C. Chen,* Virginia Tech*, Y. Yu, L. Cao,* North Carolina State University*,* ***Chenggang Tao***, Virginia Tech

Atomically thin molybdenum disulfide (MoS_2) and nanostructures have been the subject of intense research efforts for their fascinating properties and potential applications in future electronic and optical devices. Especially, monolayer MoS_2, an atomically thin semiconductor with a direct band gap, as opposed to an indirect band gap in bulk MoS_2, has been demonstrated as field effect transistors, optoelectronic devices and chemical sensors. In our experimental study, Monolayer MoS_2 and MoS_2 triangular nanostructures are synthesized through a self-limiting chemical vapor deposition (CVD) approach. The precursor materials, $MoCl_5$ and sulfur, react at high temperatures to produce MoS_2 species and subsequently precipitate onto substrates to yield MoS_2 films and triangular nanostructures. Using scanning tunneling microscopy (STM), we have investigated the structural and electronic properties of monolayer MoS_2 grown on glassy carbon and triangular MoS_2 nanostructures on highly ordered pyrolytic graphite (HOPG). We will also discuss our scanning tunneling spectroscopy (STS) measurements on these structures.

4:40pm **2D+AS+HI+MC+NS+PS+SP+SS-TuA8 Surface Characterization of Metal Oxide Layers Grown on CVD Graphene and Spin Precession Measurements**, ***Akitomo Matsubayashi***, University at Albany-SUNY*, W. Nolting,* University of Albany-SUNY*, D. Sinha,* University at Albany-SUNY*, A. Jayanthinarasimham, J.U. Lee,* University of Albany-SUNY*, V.P. LaBella*, University at Albany-SUNY

Ultra thin metal oxide films grown on graphene can be utilized as dielectric barriers between metals and graphene to help isolate a metal contact from the graphene channel for device applications. This is particularly important for graphene based spintronic devices as tunnel barriers between the ferromagnetic metal as a spin injector and graphene have been known to increase the spin relaxation time measured utilizing non-local detection technique of spin precession by avoiding the conductivity mismatch problem. However, simply depositing metal oxide layers such as aluminum oxide on graphene results in non-uniform film lowering the quality of the interface barrier. We will present a systematic study of aluminum oxide layers grown on CVD graphene under ultra-high vacuum conditions with and without titanium seed layers. The aluminum oxide layers with the 0.2 nm titanium seed layers showed reduced surface roughness. The chemical and structural composition determined by XPS will be also presented that shows full oxidation of the aluminum and partial oxidation of the titanium. The I-V characteristic study performed to electrically evaluate the metal oxide and the preliminary results of non-local spin precession measurements will be also addressed.

5:00pm **2D+AS+HI+MC+NS+PS+SP+SS-TuA9 Morphology of CVD-grown Hexagonal Boron Nitride on Cu Foils**, ***Karthik Sridhara***, *W.G. Cullen,* University of Maryland, College Park*, J.K. Hite,* Naval Research Laboratory*, M.S. Fuhrer,* Monash University, Australia*, D.K. Gaskill, B.N. Feigelson*, Naval Research Laboratory

Hexagonal boron nitride (h-BN) has grown into prominence as a dielectric for graphene heterostructures. h-BN and graphene have been grown using chemical vapor deposition on various transition metal substrates. Compared to graphene, the morphology of CVD-grown h-BN on Cu has not been as widely studied. Here, we present a systematic study of the morphology of hexagonal boron nitride (h-BN) grown on polycrystalline Cu foils by chemical vapor deposition. The growth of h-BN is performed at ~1000°C in atmospheric pressure CVD with Ammonia Borane (H3NBH3) as the precursor. The copper foils, used as catalytic substrates, are thermally annealed at ~1030°C for >5 hours prior to growth and cooled slowly following growth termination. We utilized Ultra-high vacuum Scanning Tunneling Microscopy (STM), ambient AFM and SEM to assess the morphology of the CVD grown h-BN films. Highly symmetric single crystallites of h-BN are observed for sub-monolayer growth, in agreement with recent reports. We consistently observe a corrugated topographic structure within the h-BN crystallites which is distinctly different from the surrounding copper surface, and this is consistently seen in STM, AFM, and high-resolution SEM. Our aim is to understand the nature of this difference and whether it might be due to effects of differential thermal contraction between h-BN and copper. However, complications arise due to possible changes in the copper substrate topography post-growth due to surface oxidation of the copper. Preliminary results with lateral force microscopy (LFM, frictional mode) show that these corrugations are unidirectional in a single Cu grain irrespective of the orientation of the h-BN crystal and generate frictional forces 200% greater than on the surrounding copper surface, reminiscent of earlier reports of unique frictional behavior in atomically-thin membranes [1]. STM and AFM are also used to study the twin crystal boundaries of h-BN. Preliminary STM observations indicate that merging h-BN crystals consistently have a gap of about 5 nm between them. The results of this study are independent of small variations of growth conditions.

References:

[1] C. Lee, Q. Li, W. Kalb, X.-Z. Liu, H. Berger, R. Carpick, and J. Hone, “Frictional characteristics of atomically thin sheets,” Science (New York, N.Y.), vol. 328, no. 5974. pp. 76–80, 01-Apr-2010.

5:20pm **2D+AS+HI+MC+NS+PS+SP+SS-TuA10 Influence of Chemisorbed Oxygen on the Growth of Graphene on Cu(100) and Cu(111) by Chemical Vapor Deposition**, ***EngWen Ong***, University at Albany-SUNY, *Z.R. Robinson*, U.S. Naval Research Laboratory, *T.R. Mowll, P. Tyagi*, University at Albany-SUNY, *H. Geisler*, SUNY College at Oneonta, *C.A. Ventrice, Jr.*, University at Albany-SUNY

The influence of chemisorbed oxygen on the growth of graphene by catalytic decomposition of ethylene in an ultra-high vacuum (UHV) chamber on both the Cu(100) and Cu(111) surfaces has been studied. A custom UHV compatible heater stage was constructed that allows heating of a crystal to temperatures as high as 1000 °C at hydrocarbon pressures of up to 100 mTorr. System recovery to the low 10^{-10} Torr range is achieved within a few minutes of opening the gate valve to the turbo pump. The crystal structure of the graphene films was characterized with in-situ low energy electron diffraction (LEED), and the growth morphology was monitored by ex-situ scanning electron microscopy (SEM). For the clean Cu(100) substrate, heating from room temperature to the growth temperature while dosing with ethylene resulted in the formation of epitaxial graphene films. The crystal quality was found to depend strongly on the growth temperature. At 900 °C, well-ordered two-domain graphene films were formed. For the Cu(111) surface, heating from room temperature to the growth temperature while dosing with ethylene did not result in the formation of graphene. This is attributed to the lower catalytic activity of the (111) surface and the relatively high vapor pressure of the Cu surface. The use of an Ar overpressure to suppress Cu sublimation during the growth resulted in the formation of predominately single-domain epitaxial graphene films. Predosing either the Cu(100) or Cu(111) surface with a chemisorbed layer of oxygen before graphene growth was found to adversely affect the crystal quality of the graphene overlayers by inducing a much higher degree of rotational disorder of the graphene grains with respect to the substrate. The SEM analysis revealed that the nucleation rate of the graphene islands dropped by an order of magnitude after predosing either the Cu(100) or Cu(111) surface with a chemisorbed oxygen layer before growth. On the other hand, the average area of each graphene island was observed to increase by at least an order of magnitude. Therefore, the presence of oxygen during graphene growth affects both the relative orientation and average size of grains within the films grown on both substrates.

5:40pm **2D+AS+HI+MC+NS+PS+SP+SS-TuA11 Novel Materials Properties at Atomically Thin Limit**, ***Zhi-Xun Shen***, Stanford University **INVITED**

In this talk, I will discuss recent progresses in uncovering novel materials properties at ultra-thin limit, with focus on mono-unit-cell superconductor FeSe and semiconductor MoSe2 respectively.

The observation of a large superconducting-like energy gap which opens at temperatures up to 65 K in single unit cell (1UC) thick iron selenide films on SrTiO3(FeSe/STO) has generated tremendous interest. A challenge is to understand the cause of enhanced Cooper pairing strength in this system, and possibly increase superconducting Tc. In this talk, we show angle-resolved photoemission spectroscopy, mutual inductance, and other measurements on 1UC and multi-UC thick FeSe films grown on Nb-doped SrTiO3. Our data provide clear evidence for strong cross-interface electron-phonon coupling in single UC, raising the possibility that large pairing gap are caused by the strong coupling between the FeSe electrons and certain collective modes of SrTiO3. This suggests a pathway of “integrated functional components” approach to boost superconducting properties.

The intense interest of quantum systems in confined geometries is further amplified by the recent discovery of large enhancement in photo-luminescence quantum efficiency and a potential route to “valleytronics” in atomically thin layered transition metal dichalcogenides (TMDs) MX2 (M = Mo, W; X = S, Se, Te), which are closely related to the indirect to direct band gap transition in the single layer limit. Using angle-resolved photoemission spectroscopy (ARPES) on high quality thin film samples of MoSe2 grown by molecular beam epitaxy (MBE), we have made a direct observation of a distinct transition from indirect to direct band gap as the thickness of the sample is reduced to a monolayer. The experimental band structure indicates a stronger tendency of monolayer MoSe2 towards direct band gap with larger gap size than theoretical prediction. A comparison of directly measured ARPES band gap and optical data led to important new insights on semiconductor physics in 2D. Moreover, our finding of a significant spin-splitting of ~180meV at the valence band maximum (VBM) of a monolayer MoSe2 film could greatly expand its possible application in spintronic devices.

If time permits, I will also discuss the superconductivity in CaC6 and its implication on a possible pathway for superconducting graphene.

Applied Surface Science
Room: 316 - Session AS+MC+SS-TuA

Analysis of Modified Surfaces
Moderator: Xia Dong, Eli Lilly and Company, Carl Ventrice, Jr., University at Albany-SUNY

2:20pm **AS+MC+SS-TuA1 Analysis of Surface-oxidized Polypropylene Films**, ***Mark Strobel***, *S.J. Pachuta, D. Poirier, H. Lechuga*, 3M Company **INVITED**

The most widely used industrial processes for modifying the surfaces of polymer films are flame and corona (dielectric barrier discharge) treatments. While both of these processes oxidize a thin surface region of the treated films, there are significant differences between the surfaces generated by the two surface-oxidation processes. A principal difference between corona and flame treatments is the likelihood to form water-soluble low-molecular-weight oxidized material (LMWOM). LMWOM is formed by the simultaneous oxidation and chain scission of a polymer material. LMWOM is an important surface characteristic that has a large effect on the wetting and adhesion properties of polymer surfaces.

LMWOM can be investigated by a number of surface analytical techniques, including x-ray photoelectron spectroscopy (XPS or ESCA), static secondary ion mass spectrometry (SIMS), atomic force microscopy (AFM), and contact angle measurements. This presentation will demonstrate how surface analysis enables the detection and detailed characterization of the LMWOM formed by the flame and corona treatment of polypropylene (PP) film surfaces. The mechanism of LMWOM formation can be then determined from these analytical results when coupled with an understanding of the bulk photo-and-thermal degradation of PP materials.

3:00pm **AS+MC+SS-TuA3 XPS Analysis for Modified Fabrics**, ***Christopher Deeks***, Thermo Fisher Scientific, UK, *M. Milošević, M. Radoičić, Z. Šaponjić*, University of Belgrade, Serbia, *T.S. Nunney*, Thermo Fisher Scientific, UK, *M. Radetić*, University of Belgrade, Serbia

Modifications of fabrics are becoming more important for a wide variety of applications. For example, loading TiO_2 onto cotton can improve many of the material properties, such as anti-bacterial effects, UV protection, and stain resistance.

The conformity of these modifications across sample surfaces are an important part of the application process. By using XPS in addition to other techniques, surface concentration and conformity can be determined and deduced whether the samples have met certain criteria, and how the uniformity, of lack thereof, can affect the desired outcome of the modifications.

This presentation will look at the possibility of in situ photoreduction of Ag ions on the surface of TiO_2 nanoparticles to create “active fabrics”, and will utilise XPS imaging to determine whether deposition on the surface of different fabrics has been successful.

3:20pm **AS+MC+SS-TuA4 Characterization of Corona Treated Polymers**, ***Michaeleen Pacholski***, The Dow Chemical Company

Corona treatment is often used to increase the surface energy and surface polarity of polyolefins and other polymers. In this study corona-treated, formulated polyolefin was characterized over the course of one year by SIMS, XPS and surface energy. The changes in surface chemistry could be fit to simple models to predict long-term behavior. This system is more complex than many others discussed in literature, as the formulation ingredients change in surface concentration with time, in addition to the typical decrease in surface oxygen concentration over time. SIMS and XPS measurements were used to characterize the complex surface changes as the surface energy was monitored. Additional examples of corona treated PET will also be presented.

4:20pm **AS+MC+SS-TuA7 Investigation of Atmospheric Pressure Plasma Jet as a Pre-Treatment for Adhesive Bonding of Structures Made of Carbon Fiber Reinforced Plastics (CFRP)**, ***Timo Hofmann***, *J. Holtmannspötter,* Bundeswehr Research Institute for Material, Fuels and Lubricants, Germany, *T. Meer,* Airbus Group Innovations, Germany, *J. Rehbein, G. Härtl*, Bundeswehr Research Institute for Material, Fuels and Lubricants, Germany

Carbon fiber reinforced plastics (CFRPs) are increasingly employed in novel aircraft structures due to their high tensile strength, low weight, favorable fatigue behavior, and ruggedness against outer influences (corrosion). 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 intended.

An important key factor for the success of adhesive bonding is the surface pre-treatment of the adherents. Peel-plies are commonly used for the fabrication of CFRP structures and, in theory, are said to create a pristine and uncontaminated fractured surface upon removal. In reality, the presence of release agents leads to contaminated surfaces that may cause unforeseeable failures of structures in service.

In this contribution, CFRPs (Hexcel 8552 / IM7) were produced using various peel-plies and release foils currently employed in aerospace manufacturing processes. Atmospheric pressure plasma jet (APPJ) was investigated as a method to further improve adhesion and to clean the samples from release agents.

We present a detailed investigation of the surface morphology and composition of CFRPs before and after treatment with APPJ. The peel-plies and the CFRP surfaces were examined by a combination of Field-Emission Scanning Electron Microscopy (FE-SEM), X-Ray Photoelectron Spectroscopy (XPS), and Energy-Dispersive X-ray spectroscopy (EDX).

We studied the approach of surface functionalization and contaminant removal by variation of the type of peel ply, release agent, and plasma treatment parameters. In the experiments particular focus was placed on determining changes in the chemical composition of the surface and morphology. We demonstrate that APPJ-processes offer limited cleaning capabilities for CFRP surfaces. Furthermore, the ability to induce morphological changes is highly dependent on the initial level of surface roughness and chemistry. Finally, we show that overtreatment leads to degradation of the epoxy component and enrichment of the thermoplastic portion of the matrix on the surface.

4:40pm **AS+MC+SS-TuA8 Thickness and Composition Determination of Thin Film Sn-Oxides Growth at Room Temperature using XPS Spectra**, *M. Bravo-Sanchez,* CINVESTAV-Queretaro, Mexico, ***Jorge Huerta-Ruelas***, Instituto Politecnico Nacional, Mexico, *A. Herrera-Gomez*, CINVESTAV-Queretaro, Mexico

The knowledge of the tin oxidation process is important for the development corrosion-free coatings and the engineering of alloys and compounds with specific functional properties. Tin, pure and well controlled oxidized samples were characterized by X-ray photoelectron spectroscopy (XPS). All samples were prepared on Si (100) substrates with RCA treatment before Sn deposition. The thickness of the Sn layer was approximately 100 Å as measured by a thickness monitor. The pure Sn sample was measured without ambient exposure. The oxidized samples were obtained by exposing pure Sn samples to pure oxygen at a pressure of 1×10^{-4} Torr. Three different exposure times were used: 10, 180 and 1200 seconds. To fit XPS spectra, traditional and novel method (using a double-Lorentzian) were employed to calculate thickness and composition of the oxide layer. High resolution transmission electron microscopy measurements were performed to validate calculations. Structural parameters obtained with different XPS data fitting approaches were compared, showing a clear advantage of the double-Lorentzian method in the understanding of the initial stages of tin oxidation.

5:00pm **AS+MC+SS-TuA9 Understanding the Physiochemical and Ice-Nucleation Properties of Bare and Sulfuric Acid Coated Atmospheric Mineral Dust Aerosols**, ***Manjula Nandasiri***, *N. Madaan, A. Devaraj, G.R. Kulkarni, T. Varga, V. Shutthanandan, S.A. Thevuthasan*, Pacific Northwest National Laboratory

The relationship between atmospheric aerosols and the formation of clouds is among the most uncertain aspects in our current understanding of climate change. Especially, ice and mixed-phase clouds have been less studied even though they have extensive global coverage and dominate precipitation formation. As a result, the climatic impact of ice-containing clouds is not well-understood and there is urgent need to improve ice nucleation formulations in climate models. In order to understand this phenomenon, ice nucleation experiments and parameterization development need to be carried out. Specifically, heterogeneous ice nucleation processes are sensitive to surface properties of atmospheric aerosols, which can accumulate sulfates and organics during atmospheric transport. Thus, here we investigated the physical and chemical properties on the surface of a mixed mineral dust aerosol: Arizona test dust (ATD) and kaolinite mineral dust aerosol particles that trigger ice formation.

In this study, bare and sulfuric acid coated ATD and kaolinite particles were characterized using advanced spectroscopy and microscopy techniques. These particles were reacted with sulfuric acid with different strengths in a systematic way to obtain uniform coatings on the particle surface. Following the acid reaction, the surface composition, chemical state, and elemental mapping of ATD and kaolinite particles were studied using X-ray photoelectron spectroscopy (XPS) and XPS imaging techniques. XPS showed significant changes in composition, chemical state, and elemental distribution of Si and Al on the surface of ATD and kaolinite particles due to the acid reaction. These surface properties also depend on the strength and pH value of the sulfuric acid. The surface morphology, particle size and distribution, and composition of these samples were further studied using scanning electron microscopy (SEM) combined with energy dispersive X-ray spectroscopy (EDS). The high resolution SEM micrographs showed differences in surface morphology between bare and coated samples. X-ray diffraction was also carried out to study the changes in crystallinity of ATD and kaolinite particles due to the acid coating. The samples were further characterized using atom probe tomography and transmission electron microscopy to understand the 3-D chemical distribution and microstructure, respectively. Following the characterization of physiochemical properties, ice-nucleation experiments were also carried out on ATD and kaolinite samples, which will be discussed here.

5:20pm **AS+MC+SS-TuA10 A Study of the Effect of Deep UV (172nm) Irradiation on Polyimide Surfaces**, ***Lopamudra Das***, *M.J. Kelley*, The College of William and Mary

Polyimides have a wide range of industrial and scientific applications where changes in surface structure due to UV radiation are of significant interest. Particularly in its use in spacecraft, the effect of deep UV is important to predict photo-degradation of the material. We investigated the response of commercial samples of PMDA-ODA (PI) films to 172nm UV from a xenon excimer lamp in the absence of oxygen, using XPS, ToF/SIMS, and AFM.

5:40pm **AS+MC+SS-TuA11 Small-Angle/Wide-Angle X-ray Scattering Investigation of Functional Materials at Inorganic-Macromolecular Interfaces**, ***Ich Tran***, *T.W. van Buuren, T.M. Willey, J.R.I. Lee, M. Bagge-Hansen, A. Noy, R. Tunuguntla, K. Kim*, Lawrence Livermore National Laboratory

Development in nanoscale engineering has enabled bioelectronics that can mimic and/or interact with the biological systems. Lipid bilayer-functionalized Si nanowires are considered as a promising candidate for the construction of bio-nanoelectronic devices. These biomimetic lipid bilayers serve as a general host matrix for bio-functional components such as membrane proteins. Though meaningful technological advancements have been made, critical questions still remain, in particular on structural characteristics of lipid bilayers at the interface with inorganic nanomaterials. Small-angle and wide-angle x-ray scattering (SAXS/WAXS) techniques are used to investigate self-organizations of dioleoyl-phosphatidylcholine (DOPC) lipid bilayers on Si nanowires. Critical structural parameters of the lipid bilayers (lamellarity, bilayer thickness and packing order of lipid molecules) are obtained through analyzing SAXS-derived Electron Density Profile (EDP). A decrease in bilayer thickness and a packing disorder of the lipid head groups in adjacent to supported Si nanowires have been observed upon coating on Si nanowires. Furthermore, effects on the packing order of lipid hydrocarbon tails induced by the incorporations of proteins or carbon nanotubes into lipid bilayers (served as natural or artificial ion channels, respectively) have been identified and characterized. The results shed light on a number of unresolved questions that are crucial for the comprehensive understanding this class of materials.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

In-Situ Spectroscopy and Microscopy Focus Topic
Room: 313 - Session IS+AS+MC+SS-TuA

Environmental Electron Microscopies
Moderator: Jorge Boscoboinik, Brookhaven National Laboratory

2:20pm **IS+AS+MC+SS-TuA1 Nanocrystal Shape Evolution during Growth**, ***Haimei Zheng***, Lawrence Berkeley Lab, University of California, Berkeley **INVITED**

An understanding of nanocrystal shape control mechanisms during growth is critical for the design of novel functional materials with surface-enhanced properties. However, the atomic level shape evolution of nanocrystals during growth is mostly unknown due to the lack of direct observation. We use liquid cells under transmission electron microscope (TEM) to study the growth of Pt or Pt-alloy nanoparticles in situ, where growth either by nanoparticle attachment or by monomer attachment has been observed. First, I will present Pt-Fe nanorods formation by shape-directed nanoparticle attachment under the electron beam. Winding polycrystalline nanoparticle chains are achieved at the early stage then they are straightened to yield single-crystal nanorods. Tracking their growth trajectories allows us to distinguish the force fields exerted by single nanoparticles and nanoparticle chains. Second, I will show the observation of platinum nanocube growth and the facet development. By in situ imaging with high spatial and temporal resolution, we have identified unique growth mechanisms that cannot be predicted by Wulff construction or other existing growth theorems. We found layer-by-layer growth of the {100} and {111} facets while the {110} facets show steps. We also found that the growth rates of these facets are similar until the {100} facets stop growth. Hence, the distance from {100} facets to the crystal center is fixed throughout the subsequent growth. The {110} facets are eliminated when two adjacent {100} facets meet. Lastly, the growth of {111} facets fills the corners to complete a nanocube. Our calculation suggests oleylamine ligand mobility on the facet is responsible for the arresting of {100} growing facets. References:

1. Liao et al. ¬“Facet Development during Platinum Nanocube Gro¬¬wth” Science in review.

2 . H. G. Liao, L. Cui, S. Whitelam, H. Zheng, "Real time imaging Pt3Fe nanorod growth in solution." Science 336, 1011 (2012).

3. We used TEM facility at National Center for Electron Microscopy of Lawrence Berkeley National Laboratory (LBNL), which is supported by the Office of Basic Energy Sciences, Division of Materials Sciences and Engineering of the U.S. Department of Energy under Contract #DE-AC02-05CH11231. H.Z. thanks the support of DOE Office of Science Early Career Research Program.

3:00pm **IS+AS+MC+SS-TuA3 Microfluidic Cell for *In Situ* Scanning Electron Microscopy of Hydrated Dynamic Systems**, ***Christopher Brown***, *A. Yulaev, A. Kolmakov*, National Institute of Standards and Technology (NIST)

The ability to conduct nanoscale imaging of fluid hydrated dynamic systems is a long sought goal within the scientific community. While improvement of commercial instrumentation and environmental cells has enabled in situ imaging of fluid hydrated systems using transmission electron microscopy (TEM) at the nanoscale, additional opportunities exist in implementing in situ techniques within scanning electron microscopy (SEM) instruments equipped with fluidic cells. Factors that motivate this work include: ubiquity and reduced cost of SEM instrumentation compared to TEM, drastically reduced restrictions on the sample size, and greater flexibility of systems and detectors designed for the SEM compared to TEM.

In this communication we report on development of the microfluidic environmental cell designed for in situ studies of fully hydrated dynamic objects. We describe strategies and experimental results that enable improved in situ imaging using the SEM, including development of electron transparent graphene windowed devices that increase signal-to-noise ratio of images of fluid hydrated objects. Limiting factors of in situ imaging of hydrated samples within the SEM are discussed including radiolysis and decreased electron beam penetration into liquid cells compared to higher acceleration voltage electron microscopy modalities.

3:20pm **IS+AS+MC+SS-TuA4 Liquid Jet –X-ray Photoelectron Spectroscopy and MD Simulations indicate that Li Cations in Aqueous Solutions Exhibit High Surface Propensity**, ***Kathryn Perrine***, *M.H.C. Van Spyk, M.J. Makowski, A.C. Stern, K. Parry, D.J. Tobias,* University of California Irvine, *A. Shavorskiy, H. Bluhm,* Lawrence Berkeley National Laboratory, *B. Winter,* Helmholtz-Zentrum Berlin für Materialien und Energie/Elektronenspeicherring BESSY II, Germany, *J.C. Hemminger*, University of California Irvine

Ions impact chemistry at the aqueous liquid/vapor interface in environmental chemistry, electrochemistry and biomolecular chemistry. Ions are characterized as structure makers or breakers for protein mixtures, and the trend is known as the Hofmeister series.[1] The Born electrostatic model of ions at interfaces has shown that ions should be repelled from the liquid/vapor interface due to a decrease in free energy when solvation by water occurs.[2] Molecular dynamic (MD) simulations and recent experimental studies have shown that anions tend to adsorb to the liquid interface in an inverse Hofmeister trend.[3, 4] Our synchrotron based XPS studies carried out over the last five years have provided experimental evidence that most cations follow classical ionic solution behavior and are repelled from the liquid/vapor interface, whereas some anions exhibit significant propensity for the surface. In this talk we present our recent experiments on Li salt solutions. Our experiments indicate that unlike larger cations, Li^+ is not repelled from the interface and has a significant surface propensity.

Liquid jet-X-ray photoelectron spectroscopy (LJ-XPS) is used to explore the relative ion concentrations at different depths in aqueous salt solutions. Low photoelectron kinetic energies are used to probe the surface of solutions yielding relative ionic concentrations that are present at the liquid/vapor interface. Higher photoelectron kinetic energies probe deeper into the bulk of aqueous solutions. The relative ionic concentrations of solutions prepared from lithium halide salts are compared to potassium halide solutions at different depths. MD simulations support our studies and suggest that Li^+ cations have interfacial propensity due to factors such as the tight water solvation shell on the Li^+ ions. Density profiles reveal anion and Li^+ ion adsorption to the liquid/vapor interface. In addition, we also compare various concentrations of KI and LiI aqueous solutions to determine ion adsorption at the aqueous interface.

1. K. D. Collins and M. W. Washabaugh, *Quarterly Reviews of Biophysics*, 1985, **18**, 323-422.

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4:20pm **IS+AS+MC+SS-TuA7 Complementary Microscopy and Spectroscopy Investigations of the Initial Oxidation Stages of Binary Alloy Thin Films**, ***Judith Yang***, University of Pittsburgh **INVITED**

The transient stages of oxidation – from the nucleation of the metal oxide to the formation of the thermodynamically stable oxide – represent a scientifically challenging and technologically important terra incognito. These issues can only be understood through detailed study of the relevant microscopic processes at the appropriate length scale in situ. We are studying the dynamics of the initial and transient oxidation stages of a metal and alloys with complementary in situ methods - ultra-high vacuum (UHV) transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). We have previously demonstrated that the formation of epitaxial Cu2O islands during the transient oxidation of Cu and Cu-Au thin films bear a striking resemblance to heteroepitaxy, where the initial stages of growth are dominated by oxygen surface diffusion and strain impacts the evolution of the oxide morphologies. We are presently investigating the early stages of oxidation of binary alloys where both elements compete to oxidize. Specifically, we are studying Cu-Ni and Ni-Cr single crystal thin films as a function of relative concentration, oxygen partial pressures and temperatures. For Cu-Ni oxidation, the addition of Ni causes the formation Cu2O and/or NiO where the oxide type(s) and the relative orientation with the film depend on the Ni concentration, oxygen partial pressure and temperature. For Ni-Cr model alloys containing 4, 8 and 16 at.% Cr and isothermally oxidized at 600°C and 10-7 to 10-3 torr O2 pressure, our XPS experiments reveal that after 2 min of oxidation only Cr2O3 forms on the surface of all three alloys. However, with further exposure (i.e., 30 min or 2 h), a competitive growth between Cr2O3 and NiO under all the tested conditions is clear. These XPS data are remarkable results, since prior studies reported in the literature suggest that NiO + internal Cr2O3 or NiO/NiCr2O4/Cr2O3+ internal Cr2O3 should form at least for the lower Cr content (4 and 8%) alloys. These experiments will be complemented with electron microscopy of scale cross sections to better understand the competitive nucleation and growth processes as a function of the oxygen partial pressure.

5:00pm **IS+AS+MC+SS-TuA9 Direct Observation of Structure Controlled Carbon Growth by Environmental TEM**, *J. Kling, T.W. Hansen,* ***Jakob Wagner***, Technical University of Denmark **INVITED**

In order to meet the increasing demand of faster and more flexible electronics and optical devices and at the same time decrease the use of the critical metals, carbon based devices are in fast development. Furthermore, the rich resource of carbon element limits the need for recycling and the material supports the friendly environment approach.

Layered carbon structures spanning from graphene to few layered graphite are used for extremely compact devices with outstanding performance [1,2]. A relative cheap and easy way to produce layered carbon structures on the large scale is via chemical vapor deposition (CVD) growth on catalysts like copper and nickel. However, the exact growth mechanism is still under debate and is most likely dependent on precursor pressure and growth temperature.

Here, we have used environmental transmission electron microscopy (ETEM) to follow the growth of layered structures directly at the atomic level and thereby coupling growth rate and quality of the material on the local scale to the growth parameters. Acetylene and methane are exposed to the catalyst (Ni or Cu) in situ in the microscope at pressures ranging from 0.1Pa 100Pa at temperatures ranging from 500-700C. Following the subsequent appearance of carbon layers allows for determination of instant growth rates under controlled conditions.

Single walled carbon nanotube (SWCNT) based electronics is another way of addressing the environment friendly approach of faster and better electronics. In order to exploit the potential of SWCNTs in the electronic industry fully, selective growth of either conducting or semiconducting tubes is of high importance. Growing the tubes in situ in the ETEM under relevant growth conditions gives fundamental insight in the parameters controlling the chirality and thereby the electronic properties of the SWCNTs.

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5:40pm **IS+AS+MC+SS-TuA11 *In Situ* Energy Loss Spectroscopy, A Novel Approach to the Characterization of Surfaces during MBE Growth**, ***Philippe Staib***, Staib Instruments, Inc.

A new energy analyzer for Auger Electron Spectroscopy (AES), the Auger Probe, is able to operate in growth vacuum chambers to measure *in-situ during growth* the composition of the surface [1,2,3]. The primary beam is provided by the RHEED electron gun at a very grazing incidence angle (2 to 3 degrees). The analyzer is also used in EELS mode to measure Characteristic Energy Losses (CEL). The use of a grazing incidence angle strongly enhances the strength of the energy losses peaks, which become more prominent than the elastic line

EELS data from the Auger Probe are presented showing the evolution of the CEL distributions during oxidation (ZnO), during thermal de-oxidation of GaSb, and during growth of binary and ternary materials (GaAsSb). Surprisingly, even during deposition of homoepitaxial layer, the CEL distributions show a marked dependence upon the flux of material to the sample which can reflect the formation of physi- rather than chemisorbed layers and the smoothness of the surface [4].

The CEL spectra cannot be interpreted simply, due to the strong overlapping of multiple excitations of single energy losses. A model is presented that takes into account the probability distribution for multiple losses, and allows extraction of the elementary energy loss lines from the distribution. Using this model, accurate energy loss values can be measured and an effective electron density can be calculated. The intensity of the extracted energy losses versus the intensity of the elastic peak is a measure of the ratio d/ l between the electron path length d and mean inelastic free path l of the specific loss. The inelastic mean free path for each loss line can be deducted using d values from monte-carlo simulation of the electron trajectories and the intensity ratio of the loss peak vs. elastic peak.

Special thanks to S. Svensson and W. Sarney of ARL for their collaboration during measurements used in this work.

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6:00pm **IS+AS+MC+SS-TuA12 Selective Staining for Enhanced Spectroscopic Identification of Domains in Immiscible Polymer Blends by Micro-Raman Spectroscopy**, ***Nicholas Heller****, C.R. Clayton,* SUNY Stony Brook*, S.L. Giles, J.H. Wynne,* Naval Research Laboratory*, M.J. Wytiaz, M.E. Walker*, Sherwin-Williams Company

Blends of incompatible polymers combined with fillers and pigments were used to produce unique low reflectance thermoset coatings. Understanding the origins of low reflectance from the coatings was approached through microscopy, thermal analysis and spectroscopic analysis of both pigmented and control clear coatings. Polymeric phase separation was confirmed by the presence of two distinct glass transition temperatures. Microscopy revealed random surface features for the pigmented coatings. Therefore, the pigments and fillers were removed to observe the polymer-polymer interactions within the blend under curing conditions. Identification of the polymeric domains was obtained using Raman spectroscopy mapping of cross-section samples embedded within a polyester resin. Cross-section samples of coatings were utilized to isolate encapsulated polymer domains from the continuous polymer network to minimize spectral averaging from both domains. Raman analysis of the blends was compared to cured films generated using the individual resins. The embedding process produced a marker peak in one phase and in one individual resin. The marker peak was found to be from styrene monomer and was found to selectively bind to one component of the polymer blend, based on polar and hydrogen bonding characteristics..

Nanometer-scale Science and Technology
Room: 304 - Session NS+AS+SS-TuA

Nanowires and Nanotubes: Advances in Growth and Characterization
Moderator: Lincoln Lauhon, Northwestern University

2:20pm **NS+AS+SS-TuA1 Surface Chemical Choreography of Nanowire Synthesis**, ***Michael Filler****, S.V. Sivaram, N. Shin, I.R. Musin*, Georgia Institute of Technology **INVITED**

This talk will provide an overview of our recent efforts to understand the chemical phenomena underlying semiconductor nanowire growth. The vapor-liquid-solid technique – where a liquid "catalyst" droplet collects atoms from the vapor and directs crystallization of individual solid layers – is a ubiquitous method for the synthesis of these quintessential nanoscale building blocks, but a lack of atomic-level design rules prevents robust programming of structure. Long-standing challenges in the control of heterostructure, dopant profile, atomic stacking sequence, kinking, and even simple axial growth restrict the accessible property space and highlight the pitfalls of an overreliance on empirical process optimization. We couple in-situ or operando infrared spectroscopy with post-growth high-resolution electron microscopy to connect specific surface chemical bonds present during synthesis with nanowire structure. Studies of Si and Ge nanowires demonstrate the fundamental, and previously unrecognized, role of adsorbed hydrogen atoms. The surface coverage of these precursor (e.g., Si_2H_6 or Ge_2H_6) decomposition intermediates, which we quantitatively determine as a function of pressure and temperature, can change over a narrow range and strongly influence growth. Our findings show, for example, that adsorbed hydrogen is essential for stabilizing the catalyst or driving elongation in new crystal directions for Ge and Si nanowires, respectively. We leverage these insights to rationally design precursors that choreograph nanowire structure on multiple length scales, permitting the fabrication of user-defined defect, kinking, and diameter-modulated superstructures.

3:00pm **NS+AS+SS-TuA3 Atom Probe Tomography Analysis of GaAs-AlGaAs Core-Shell Nanowire Heterostructures**, ***Nari Jeon***, Northwestern University*, S. Morkötter, G. Koblmüller,* Technische Universität München, Germany*, L.J. Lauhon*, Northwestern University

GaAs-AlGaAs planar heterostructures have various electronic and optoelectronic applications such as solar cells and light-emitting diodes.[1-2] This is due to a small lattice mismatch between GaAs and AlAs providing wider opportunities in bandgap tuning. Moreover, modulation doping scheme is well-known to be effective in enhancing electron mobility in the heterostructures by minimizing electron scattering from ionized impurities. Since growth of GaAs-AlGaAs core-shell nanowires was demonstrated in 2005,[3] there has been a growing number of papers reporting novel (opto)electronic transport properties, which are originated from the nonparallel geometry of GaAs-AlGaAs interfaces and its related compositional fluctuations.[4] In fact, compositional structures are more complex in the core-shell nanowires compared to the planar counterparts. For example, there are six Al-rich bands along the corners of {110} sidewall facets in the AlGaAs shell.[5] While most of the previous studies were based on transmission electron microscopy on cross-sectioned samples, we exploited the atom probe tomography (APT) to explore compositional fluctuations in three dimensions. The focus of the presentation will be APT sample preparation and composition characterization of Si delta-doped GaAs-AlGaAs core-shell nanowires. Molecular beam epitaxy reactor was used to grow the core-shell nanowires and the GaAs-AlGaAs superlattice planar samples as a reference to the nanowires. Individual nanowires were mounted on tungsten tips using micromanipulator for APT and planar samples were fabricated into tip-shaped APT samples by the lift-out and sharpening method using focused ion beam (FIB). Carefully designed structures of the superlattice with varied thickness and spacing in planar samples enabled us to estimate the range of possible ion beam damage from FIB. The atom probe conditions such as laser pulse energy and target detection rate were also optimized to achieve high spectral and spatial resolutions, which are critical for APT of III-V compound semiconductors where preferential detection loss and surface diffusion for III and/or V group elements are possible depending on the APT conditions. Intermixing at GaAs-AlGaAs interface and stoichiometric fluctuation in AlGaAs shell were mainly studied along with the detection limit of Si dopants in the delta doping layer.

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3:20pm **NS+AS+SS-TuA4 Scanning Tunneling Microscopy of Semiconductor Nanowire Surfaces and Devices**, *R. Timm, J. Knutsson, M. Hjort, S. McKibbin, O. Persson, J.L. Webb*, ***Anders Mikkelsen***, Lund University, Sweden

III-V semiconductor nanowires (NWs) offer tremendous possibilities for device application in solid-state lightning, energy conversion, and information technology [1]. With their small diameter and their very large surface-to-volume ratio, the NW device behavior is strongly determined by their surface structure. Thus, it is both essential and challenging to investigate their atomic surface structure and to combine this information with electrical measurements on individual NWs.

Recently, we have managed to clean InAs NWs from their native oxide and revealed the atomic arrangement of their side surfaces with scanning tunneling microscopy (STM). Here, we present STM images of various NW surfaces of both wurtzite and zincblende crystal structure [2], including InAs, GaAs, InP, and InSb NWs. By combining STM imaging with scanning tunneling spectroscopy (STS) measurements, we simultaneously study the surface structure and local electronic properties across the interfaces of NW heterostructures [3].

For correlating local structural and electronic characterization with transport measurements of NW devices, we have developed a novel STM-based setup: We are using combined atomic force microscopy (AFM) and STM/S on individually contacted NWs for mapping the surface structure and the local band alignment along the NW heterostructure under device performance. We show initial results of this unique approach on InAs-GaSb nanowire tunnel diodes, where we could prove Esaki behavior of a NW while it was investigated by STM/AFM. From a set of STS spectra we determined the position of the Fermi level along the nanowire for different applied biases, showing an abrupt drop directly at the material interface. In a reverse experiment, we used the STM/AFM tip as local gate and measured the resulting source-drain current through the nanowire for different biases [4].

In some cases it is desirable to measure the conductivity of individual as-grown nanowires in an upright-standing configuration without any sample processing. Here we have developed an alternative setup where the STM tip is used to first image free-standing nanowires from top and then form a point contact [5]. We will demonstrate the reproducibility of this method in establishing low-resistive Ohmic contacts to individual InP and InAs nanowires [6], and we will show initial results on the I-V properties of individual InP NW solar cells.

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4:20pm **NS+AS+SS-TuA7 Poly-Aromatic Hydrocarbon Nanostructure Growth on Single and Multi-Layer Graphene**, ***Alexander Yulaev***, CNST/UMD Graduate Student Researcher, *A. Kolmakov*, NIST

Poly-aromatic hydrocarbons (PAH) are known as potential hazardous organic pollutants, which can be found in soil, air, meat, fish and etc. Carbon based materials are routinely used for environmental remediation. Graphene has ultrahigh surface area and can be seen therefore as an "ultimate carbon filter". In our communication we report PAH nanostructure nucleation and growth on a single and multi-layer graphene CVD grown on a copper substrate. The PAH deposition was performed by thermal evaporation in vacuum, and resultant morphology of a PAH was studied by means of SEM as a function of time, rate, substrate temperature and graphene thickness. We found that PAH predominantly grows in a form of nanowires which have a good vertical alignment with respect to a graphene plane. It was shown that temperature of a substrate, deposition rate of PAH, and number of graphene layers were the key parameters to control the PAH morphology such as a nucleation density and diameter of PAH nanowires. We relate the orthogonal growth of PAH nanowires to the discotic nature of PAH molecules forming weak VDW interactions with a graphene basal plane and lamella like structures due to favorable face-to-face intermolecular interaction. We envision PAH nanostructures grown on a graphene substrates may help optimize PAH filters.

4:40pm **NS+AS+SS-TuA8 Using Surface Chemistry to Direct the *In Situ* Synthesis and Placement of Nanowires**, *A.A. Ellsworth, J. Yang, Z. Shi*, ***Amy Walker***, University of Texas at Dallas

Nanoscale one-dimensional materials, commonly called nanowires, have properties that differ significantly from their bulk counterpart materials, and thus have applications in areas including sensing, energy conversion, electronics and optoelectronics. One of the major challenges in the practical use of nanowires is their integration into complex functional structures in a predictable and controlled way. We have recently introduced two promising new techniques by which to direct the growth of metallic and semiconducting nanowires. ENDOM, or Electroless Nanowire Deposition On Micropatterned substrates, employs electroless deposition (ELD) to form metallic nanowires on substrates. SENDOM, or Semiconductor Nanowire Deposition on Micropatterned surfaces, uses chemical bath deposition (CBD) to deposit semiconductor nanowires. SENDOM and ENDOM are generally applicable to the preparation of metallic, semiconducting, and even insulating nanostructures on many technologically relevant substrates. These techniques have several advantages over existing *in situ* synthesis and placement methods: it is fast, and it does not require expensive lithographic equipment or a clean room.

Using ENDOM or SENDOM we are able to create nanowires that are ultralong (centimeters) and follow complex paths such as a right-angle or a curve. We illustrate ENDOM by deposition of Ni, Cu, Pd and other nanowires on patterned –OH/–CH_3 SAMs. We exploit the different deposition rates electroless deposition of metals using dimethylamine borane (DMAB) on –CH_3 and –OH terminated SAMs to deposit nanowires. We illustrate SENDOM by deposition of CuS nanowires on patterned –COOH/–CH_3 SAMs. In this case, the deposition is controlled by the interaction of thiourea (sulfur source) with the SAM surface. In this paper we discuss the reaction pathways involved in the formation of these nanowires including the nucleation sites and the dependence of the nanowire growth on pH and deposition temperature.

5:20pm **NS+AS+SS-TuA10 Development of New Nanocatalysts through Restructuring of Co_3O_4 Nanorods Anchored with Pt Atoms**, ***Shiran Zhang***, University of Notre Dame, *A. Frenkel*, Brookhaven National Laboratory, *F. Tao*, University of Notre Dame

Low-temperature water-gas shift (WGS) reaction is crucial for low-temperature fuel cell technology as it provides a solution for on-board hydrogen purification near operational temperature. Design of catalysts with lower activation energy and higher activity is critical for a practical application. Significant effort has been devoted to development of new WGS catalysts with high activity at low temperatures. Most of them are metal nanoparticles supported on reducible oxides such as CeO_2 or TiO_2.

Here we reported two nanocatalysts, $PtCo_n/Co_3O_4$ and $Pt_mCo_{m'}/CoO_{1-x}$ that are highly active for low-temperature WGS reaction. They were prepared by restructuring singly dispersed Pt atoms supported on Co_3O_4 nanorods through a controlled reduction. The single dispersion of Pt atoms on cobalt oxide nanorods was confirmed with high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). Photoemission feaures of Co2p and Pt $4d_{5/2}$ of these catalysts during catlaysis were tracked with ambient pressure x-ray photoelectron spectroscopy (AP-XPS) using monochromated Al Kα. Coordiantion environment of Pt atoms was tracked with in-situ extended x-ray absorption fine structure spectroscopy

(EXAFS). These ex-situ and in-situ studies show that two new active phases, $PtCo_n/Co_3O_4$ and $Pt_mCo_{m'}/CoO_{1-x}$ were formed in the temperature ranges of 150 °C – 200 °C and 280 °C – 350 °C in the mixture of 3 Torr CO, 1 Torr H_2O, respectively. The formation of singly dispersed bimetallic sites $PtCo_n$ anchored on Co_3O_4 was confirmed with in-situ EXAFS studies. The formed $Pt_mCo_{m'}$ nanoclusters supported on CoO_{1-x} in the temperature range of 280 °C – 350 °C was identified with HAADF-STEM. Kinetics studies in the gas mixture of carbon monoxide and water vapor with a ratio of 3:1 revealed that activation barriers for $PtCo_n/Co_3O_4$ at 150-200 °C and $Pt_mCo_{m'}/CoO_{1-x}$ at 150-250 °C are 50.1±5.0 kJ/mol and 29.6±4.0 kJ/mol, respectively. Turn-over frequencies (TOFs) of the two new catalysts $PtCo_n/Co_3O_4$ and $Pt_mCo_{m'}/CoO_{1-x}$ at 150 °C are larger than those of Pt and Au nanoparticles supported on CeO_2 and TiO_2 catalysts by one magnitude. The excellent activities of the new catalytic phases $PtCo_n/Co_3O_4$ and $Pt_mCo_{m'}/CoO_{1-x}$ formed through restructuring the singly dispersed Pt atoms on Co_3O_4 suggest a method of developing new catalysts through restructuring singly dispersed catalyst atoms such as noble metals on an oxide support.

5:40pm **NS+AS+SS-TuA11 A Study of Single-Walled Carbon Nanotubes Coated with Iron Oxide (Fe_2O_3) Nanoparticles for Enhanced Magnetic Properties**, ***Suman Neupane***, *D. Seifu*, Morgan State University

Carbon nanotubes (CNTs) continue to attract significant interest due to their extraordinary thermal, electrical, optical, and mechanical properties. The preparation of CNTs coated with magnetically sensitive Fe_2O_3 nanoparticles has implications to the development of advanced heat transfer nanofluids and high capacity lithium ion batteries. In this report, single-walled carbon nanotubes (SWNTs) were uniformly coated with Fe_2O_3 nanoparticles through solution mixture. Scanning and transmission electron microscopy were used to compare the surface morphology of pristine SWNTs and as-prepared SWNTs coated with Fe_2O_3 nanoparticles. Raman spectroscopy and thermo gravimetric analysis presented the extent of defects and the amount of Fe_2O_3 nanoparticles present in the sample. Near edge X-ray absorption fine structure spectroscopy was used to probe the electronic band structure of as-prepared core-shell structures. Magnetization measurements indicate that the coercive field of SWNTs coated with Fe_2O_3 nanoparticles was twice that of pristine SWNTs.

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Surface Science
Room: 309 - Session SS+NS-TuA

Nanostructures: Growth, Reactivity and Catalysis

Moderator: Judith Harrison, United States Naval Academy, Greg Kimmel, Pacific Northwest National Laboratory

2:20pm **SS+NS-TuA1 Building Nanostructured Nanowires via Sequential Catalyst Reactions**, ***Frances Ross***, IBM T.J. Watson Research Center **INVITED**

By exposing catalytic nanoparticles to reactive source gases, nanowires can be grown with excellent control over length, diameter, crystal structure and composition. Here we discuss the degree to which this vapour-liquid-solid growth mechanism can be augmented by "programming" a sequence of reactions in the catalyst. Our aim is to produce complex structures in which quantum dots and quantum wells of precise dimensions are incorporated into single nanowires. We supply different species to nanowire catalysts, either as reactive gases or by evaporation, triggering the formation of new phases that become incorporated into the nanowires as they grow. *In situ* transmission electron microscopy allows us to view this process, identify phases and measure kinetics. As an example, we discuss the formation of silicide quantum dots within Si nanowires. Supplying metals such as Co and Ni to catalysts composed of liquid AuSi results in the formation of faceted silicide nanocrystals. These floating nanocrystals subsequently attach at the AuSi/Si interface. Further growth of Si incorporates these quantum dots into the nanowire. We discuss the generality of this phenomenon and the control of silicide structure and dimensions. The formation of narrow quantum wells, such as Ge layers within Si nanowires, can also benefit from understanding the sequential changes in the catalyst. We describe the relationship between catalyst properties and quantum well compositional abruptness, strain and stability. We finally consider the possibilities of combining quantum dots and quantum wells in single nanowires. We suggest that control of reaction pathways within the catalyst provides exciting opportunities for the growth of complex nanostructures.

3:00pm **SS+NS-TuA3 Ar/O_2 and H_2O Plasma Modified SnO_2 Nanomaterials for Gas Sensing Applications**, ***Erin Stuckert***, *E.R. Fisher*, Colorado State University

Tin oxide (SnO_2) is an excellent material for gas sensing applications. The sensing mechanism of SnO_2 is controlled through gas interactions with adsorbed oxygen, which alters the charge flow through the sensing material. By measuring changes in charge flow, sensitivity and selectivity of a gas sensor can be determined. Sensitivity is improved by increasing surface-gas interactions of high surface area materials, SnO_2 nanoparticles and nanowires, combined with surface modification. One surface modification method that can achieve greater oxygen adsorption is plasma treatment; with an expansive parameter space, plasmas allow for greater control of the modification process. In this work, commercial SnO_2 nanoparticles and chemical vapor deposition (CVD)-grown SnO_2 nanowires were plasma modified to create oxygen vacancies with the aim of increasing oxygen adsorption during sensing. Specifically, we employed Ar/O_2 and H_2O plasmas because they can etch materials like SnO_2 to increase oxygen adsorption by creating surface oxygen vacancies. Ar/O_2 plasma treatment of SnO_2 nanoparticles and nanowires showed increasing oxygen adsorption with increasing plasma power and treatment time without changing Sn oxidation state or morphology, as measured by X-ray photoelectron spectroscopy (XPS) and powder X-ray diffraction (PXRD). With low power H_2O plasma treatments, however, greater oxygen adsorption was observed with nearly complete Sn reduction as well as significant morphological changes evidenced in XPS, PXRD, and scanning electron microscopy (SEM). Plasma treated materials were evaluated for their sensitivity and selectivity for a variety of gases including ethanol, formaldehyde, and benzene. Results for both Ar/O_2 and H_2O plasma treated SnO_2 nanoparticles and nanowires will be presented and discussed with respect to their sensing capabilities, including changes in selectivity and sensitivity.

Keywords:

Plasma treatment

Gas sensor

Tin oxide

Nanowire

Nanoparticle

3:20pm **SS+NS-TuA4 Interaction of D_2O on the Surface Grown ZnO(0001) Nanostructures**, ***Xingyi Deng***, *D.C. Sorescu, J. Lee, C. Matranga*, National Energy Technology Laboratory

D_2O on the ZnO nanostructures grown on Au(111) has been investigated using a combination of experimental and theoretical methods as to probe the reactivity of model ZnO catalysts at the atomic level. We performed a series of D_2O temperature programmed desorption (TPD) experiments on two distinctive surfaces, one consisting of single layer Zn(0001) nanostructures, and the others consisting of mixtures of single and bilayer ZnO(0001) nanostructures. On the basis of our TPD data and in comparison with the ZnO structural characteristics, we are able to assign each D_2O TPD peak to a specific site existing on the ZnO nanostructures. Specifically, desorption peaks at 150 and 200 K are assigned to sublimation of D_2O multilayers and desorption of D_2O adsorbed directly on the ZnO surfaces, respectively; and D_2O adsorbed on the edges of either single or bilayer ZnO desorbs at a slightly higher temperature ~260 K. More importantly, we identify that D_2O binds to the steps between the single and bilayer ZnO much stronger than any other sites, desorbing around 400 K. Computational modeling based on density functional theory (DFT) calculations provides detailed adsorption geometry and energetics of the D_2O-ZnO(0001)/Au(111) system, further supporting our TPD assignments. Implications of our fundamental results for ZnO based catalysts will be discussed.

4:20pm **SS+NS-TuA7 2014 AVS Medard Welch Award Lecture: Quasicrystals to Nanoclusters: It's All on the Surface**, ***Patricia Thiel****, Iowa State University **INVITED**

Surface science continues as an exciting frontier—perhaps more so now than in the past—for at least two reasons. First, powerful new tools are emerging, and second, a broad and robust body of knowledge has been established which is serving as a springboard for new breakthroughs, and is critically guiding other fields. In this talk I will present some of the contributions that I and my coworkers have been privileged to make in this field, particularly in the area of quasicrystal surfaces, and in the area of growth and stability of nanoclusters and thin films at surfaces. Metallic quasicrystals have a remarkable atomic structure that engenders unusual properties, including surface properties, and our goal has been to establish the structure-property relationship at the surface. One of our achievements was to show that quasicrystal surfaces are generally bulk-terminated. This

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*** Medard W. Welch Award Winner**

laid the groundwork for showing that one of the characteristics of quasicrystals—low friction—derives (at least in part) from the quasiperiodic atomic structure. It also allowed us to understand unusual features of thin film nucleation and growth on these surfaces, and facilitated efforts of other groups to exploit quasicrystals and complex metallic alloys as catalysts. Nucleation and growth of nanoclusters and thin films also shows surprising features on more conventional (crystalline metal) surfaces, and has been a topic of investigation in my group for some time. We discovered that unusual smooth growth at low temperature, and associated non-monotonic temperature dependence of roughness, reflects a process now called "downward funneling". In addition to non-equilibrium growth morphologies, we have also explored the relaxation of these morphologies towards equilibrium. We found that two-dimensional homoepitaxial metal nanoclusters can diffuse significant distances, leading to coarsening (a reduction in the cluster density) via agglomeration. Nanocluster destabilization and coarsening can also occur via Oswald ripening, but the identity of the mass carriers may not be obvious. The presence of even trace amounts of adsorbates can lead to formation of additive-metal complexes which more efficiently transport mass than metal atoms. We have searched for these complexes under conditions which have rarely been investigated in the past, i.e. very low temperature and very low coverage, with some surprising results.

5:00pm **SS+NS-TuA9 Photodeposited Pt Nanoparticles on Iron Oxide Nanoparticles Supported on Highly Oriented Pyrolytic Graphite**, ***Jayde Kwon***, *J.C. Hemminger*, University of California Irvine

Metal-semiconductor hybrid systems have been of great interest due to their unique photocatalytic properties. In metal-semiconductor hybrid systems, semiconductors are used as light absorbing components. They absorb photons and create electron holes localized at the semiconductor, which are formed by excited electrons that move through the heterointerface. Fe_2O_3 is a promising semiconductor photocatalyst due to its visible light absorption (E_g = 2.2 eV), abundance, non-toxicity, and stability against photo corrosion. However, Fe_2O_3 suffers from short hole diffusion length, low electrical conductivity and high rate of electron hole recombination. To overcome these barriers, different transition metals (e.g. Au, Si, Pt) have been deposited on Fe_2O_3. Particularly, Pt on Fe_2O_3 is an ideal heterogeneous catalyst that has a variety of uses such as photoelectrochemical water splitting and CO oxidation. Importantly, Pt on Fe_2O_3 provides an improvement in photocatalytic properties on the degradation of dyes, such as methylene blue. Although many studies deposit Pt on various forms of Fe_2O_3 (e.g. films, nanorods, and coreshells), Pt nanoparticles on discrete Fe_2O_3 nanoparticles on highly oriented pyrolytic graphite (HOPG) has not been studied. The deposition of Pt on Fe_2O_3 has been studied using various methods such as electrodeposition and solution based synthesis. However, photodeposition of Pt on Fe_2O_3 has not yet been studied. In this work, we demonstrate photodeposition of Pt nanoparticles selectively on Fe_2O_3 nanoparticle arrays formed by physical vapor deposition on HOPG. We find that the Fe_2O_3 nanoparticles are in the range of 7-20 nm in diameter. On-going studies of the catalytic properties of these unique materials will be presented.

5:40pm **SS+NS-TuA11 Formation and Stability of and Surface Chemistry on Dense Arrays of Au Nanoclusters on Hexagonal Boron Nitride/Rh(111)**, *M.C. Patterson*, ***Phillip Sprunger***, *J.R. Frick, Y. Xu*, Louisiana State University, *B.F. Habenicht*, University of California Merced, *R.L. Kurtz*, Louisiana State University, *L. Liu*, Texas A&M University

We have studied the nucleation and growth of Au clusters at sub-monolayer and greater coverages on the h-BN nanomesh grown on Rh(111) by means of scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), and density functional theory (DFT). STM reveals that sub-monolayer Au deposited at 115 K nucleates within the nanomesh pores and remains confined to the pores even after warming to room temperature. Whereas there is a propensity of mono-atomic high islands at low temperature, upon annealing, bi- and multilayer Au clusters emerge. Deposition of higher coverages of Au similarly results in Au confined to the nanomesh pores at both 115K and room temperature. XPS analysis of core-level electronic states in the deposited Au shows strong final-state effects induced by restricted particle size dominating for low Au coverage, with indications that larger Au clusters are negatively charged by interaction through the h-BN monolayer. DFT calculations suggest that the structure of the Au clusters transitions from monolayer to bilayer at a size between 30 and 37 atoms per cluster, in line with our experiment. Bader charge analysis supports the negative charge state of deposited Au. Using vibrational EELS, CO and O_2 are used to probe the activity of these gold model catalysts.

6:00pm **SS+NS-TuA12 Collective Multi-Atom Diffusion in Ag/Ge(110) 1D Nanoisland Growth**, ***Shirley Chiang***, *C.H. Mullet,* University of California, Davis, *M.C. Tringides,* Iowa State University and Ames Lab-USDOE, *M.S. van Zijll, B.H. Stenger, E.S. Huffman, D.J. Lovinger, E.C. Poppenheimer*, University of California, Davis

The growth of Ag deposited on Ge(110) was studied with low energy electron microscopy (LEEM) and scanning tunneling microscopy (STM). The LEEM studies showed the formation of long, one-dimensional (1D) multi-height islands over the temperature range 430C-530C. During deposition, the length of the islands increases at a constant rate (~10^6 atoms/sec reaching ~20 microns) and constant width (100-200nm) for 9ML total deposition. Stochastic diffusion cannot account for these very high island growth rates. When smaller islands decay, the rate is ~$2x10^7$ atoms/sec, which is also exceedingly fast, based on the Ag diffusion and detachment barriers. These high rates are not consistent with independent adatom events and imply multi-atom correlated diffusion. Such collective mass transport must be related to the mobility of the wetting layer. STM images show the crystalline structure of the 1D Ag islands and also indicate that the reconstructed regions between the islands consist of bare Ge. These data are corroborated by LEEM IV curves. Together, they confirm that the wetting layer provides the material for the islands to grow at these high rates.

Surface Science
Room: Hall D - Session SS-TuP

Surface Science Poster Session

SS-TuP1 Visible Light Photocatalytic Degradation of Methylene Blue using Ag_2O Nanostructures, *Z.-H. Yang,* ***Szetsen Lee***, Chung Yuan Christian University, Taiwan, Republic of China

Various kinds of Ag_2O nanostructures were prepared by a precipitation reaction of silver nitrate, ammonium nitrate, and sodium hydroxide with different mixing ratios and temperatures. The band gap values of Ag_2O nanostructures were measured using diffuse uv-visible reflectance spectroscopy. The photocatalytic activity of Ag_2O nanostructures was tested with the degradation reaction of methylene blue (MB) in aqueous solutions. A halogen lamp with a cut-off filter (> 400 nm) was used as the visible light source. The intensity variation of the 664 nm absorption peak of MB was monitored. The photocatalytic degradation rate of MB varies with the shapes of Ag_2O nanocrystals. The degradation rates of MB were correlated with the measured band gap values of Ag_2O. The efficiency of visible-light photocatalytic performance of Ag_2O nanostructures is discussed.

SS-TuP3 Formation of Copper Nanoparticles on a Surface of OH-terminated ZnO Powder Material, ***Hsuan Kung***, *A.V. Teplyakov*, University of Delaware

Cu/ZnO catalyst is one of promising catalysts commonly used in industry for methanol synthesis, methanol steam reforming, and hydrogen production reactions. Two typical methods to prepare this catalyst are wet chemistry or vacuum-based techniques. In this study, we grew Cu nanoparticles on zinc oxide (ZnO) powder at room temperature using common chemical vapor deposition precursors, such as hexafluoroacetylacetonate copper(I) vinyltrimethylsilane, (Cu(hfac)(VTMS)) under high vacuum conditions. Before deposition, exposing ZnO powder to the gas-phase water to form a hydroxyl-terminated monolayer was able to enhance the growth of copper nanoparticles. In-situ FTIR studies showed that the intensity of the infrared signatures of hydroxyl groups decreased following exposure to copper precursor and confirmed copper deposition . X-ray photoelectron spectroscopy and Auger electron spectroscopy studies determined that Cu(I) species are the dominant products present on the surface. Cu nanoparticles grown on ZnO(000-1), ZnO (10-10) and defect sites were visualized by Scanning electron microscopy. This Cu/ZnO surface covered with strongly bound hfac ligands was then annealed to different temperature to remove surface contamination. The thermal chemistry involved in this process and the chemical stability of the surface-bound ligands will be discussed.

SS-TuP4 Radical Reactions with Organic Surfaces, ***Robert Chapleski***, *D. Troya*, Virginia Tech

Motivated by recent ultra-high-vacuum surface experiments, we have used electronic structure methods, quantum mechanical/molecular mechanical calculations, and molecular dynamics simulations to investigate the structure and reactions of radicals with organic surfaces.

For the first reaction being studied, that of ozone with C60 fullerene, we have characterized stationary points in the potential energy surface for the reactions of O3 with C60 that include both the formation of primary ozonide and subsequent dissociation reactions of this intermediate that lead to C–C bond cleavage. We have also investigated the addition of multiple O3 molecules to the C60 cage to explore potential reaction pathways under the high ozone flux conditions used in recent experiments. The lowest-energy product of the reaction of a single ozone molecule with C60 that results in C–C bond breakage corresponds to an open-cage C60O3 structure that contains ester and ketone moieties at the seam. This open-cage product is of much lower energy than the C60O + O2 products identified in prior work, and it is consistent with IR experimental spectra. Subsequent reaction of the open-cage C60O3 product with a second ozone molecule opens a low-energy reaction pathway that results in cage degradation via the loss of a CO2 molecule. Our calculations also reveal that, while full ozonation of all bonds between hexagons in C60 is unlikely even under high ozone concentration, the addition of a few ozone molecules to the C60 cage is favorable at room temperature.

We have also investigated the reaction of nitrate radicals with functionalized self-assembled monolayer surfaces. Specifically, using quantum mechanical/molecular mechanical calculations, we have calculated vibrational modes of nitrate-SAM products that are consistent with IR experimental spectra. Also, using molecular dynamics simulations, we are able to describe the orientation of the alkanethiol chains that form the surface in order to provide insight into reaction mechanisms under further experimental study.

SS-TuP5 Degenerate Phases of Iodine on Pt(110) at Half-Monolayer Coverage, *N. Oberkalmsteiner, M. Cordin,* ***Stefan Duerrbeck***, *E. Bertel,* University of Innsbruck, Austria, *J. Redinger,* Vienna University of Technology, Austria, *C. Franchini*, University of Vienna, Austria

Iodine-surface interactions are of considerable interest in sustainable-energy research. For instance, Iodine is used as redox shuttle in dye-sensitized solar cells and serves as a promoter in photocatalytic water splitting. In most of these applications, Pt is involved either as an electrode or as co-catalyst or both. As part of a general study of Pt-halogen interaction we discuss here the adsorption of Iodine on Pt(110) at a coverage (Θ) of 0.5 monolayers (ML). The I/Pt(110) adsorbate system was investigated by scanning tunneling microscopy (STM), low-energy electron diffraction (LEED) and by density functional theory (DFT) calculations using both, the LDA and the GGA approximation. Remarkably, three different phases involving occupation of two different binding sites were found to coexist at $\Theta = 0.5$ ML. While the observed phases are similar to the ones reported for Br on Pt(110)[1-2], the preferred binding sites are different. The structure of defects in the adsorbate layer as well as the dynamics at the transition between the nearly degenerate phases is not the same as the one in a Br layer indicating a shifted balance of adsorbate-substrate binding and inter-adsorbate repulsion. The c(2×2)->(3×2) phase transition shows evidence for a long-range interaction. The latter phase also involves a surprisingly strong buckling in the Pt surface amounting to 15% of the interlayer distance. While the DFT calculations reflect the energetic details of the c(2×2) phase with stunning precision, they only partially reproduce the experimental results from the (3×2) phase. Comparison with literature data shows that the iodine adlayer is almost floating on Au(110) and uniaxially compressible on Pd(110), while on Pt(110) Iodine adsorption is tied to specific adsorption sites, precluding the formation of compression structures.

[1] E. Doná, T. Loerting, S. Penner, et al., Physical Review Letters **98**, 186101 (2007).

[2] M. Cordin, B. A. J. Lechner, S. Duerrbeck, et al., Sci. Rep. **4** (2014).

SS-TuP6 Reaction of Hydrazine with Cl-terminated Si(111) Surface, ***Fei Gao***, *A.V. Teplyakov*, University of Delaware

This work focuses on obtaining well-defined surface of silicon functionalized with hydrazine to produce an oxygen-free platform for further functionalization. Single crystalline Si(111) surface has been prepared using modified RCA procedure to produce a well-defined H-terminated 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. Hydrazine-functionalized Si(111) sample is obtained from Cl-Si (111) surface with anhydrous hydrazine at 35°C under Ar atmosphere. To confirm the presence of Si-N bonds following this procedure and to establish the structures of surface species produced, we followed the reaction by Fourier-transform infrared spectroscopy, X-ray photoelectron spectroscopy, and time-of-flight secondary ion mass spectrometry. To study the configuration of Si-NH_x groups on the surface, result was compared with the results of phenylhydrazine reactions on Cl-terminated silicon surface by wet chemistry method and also on clean silicon surface under ultrahigh vacuum (UHV) condition. Density functional theory (DFT) calculations were performed to infer the mechanisms of surface reactions and to compare the predicted vibrational spectra and core-level energies with the results of experimental studies.

SS-TuP8 Synthesis of Formate Species on Cu Surface using CO_2 Molecular Beam, ***Tetsuya Ogawa***, *Q. Jiamei, T. Kondo, J. Nakamura*, University of Tsukuba, Japan

The methanol synthesis by hydrogenation of CO_2 attracts a great deal of attention because this process can realize the direct conversion of CO_2 into a useful chemical feedstock. In a present industrial process using Cu/ZnO-based catalyst, however, the reaction requires high pressure (50-100 bar) and high temperature (200-300°C). If this reaction proceeds at a mild reaction condition, it would be a very attractive process to convert CO_2. But the detailed process of the reaction is not well understood. We focus on the formate synthesis on Cu surfaces, which is the first step of the methanol synthesis reaction. Our previous studies suggest that this process proceeds by the translational and vibrational energy of CO_2 molecules. The kinetic analysis of formate synthesis suggests that the mechanism of the reaction can be an Eley-Rideal type, in which gaseous CO_2 directly reacts with hydrogen atoms on Cu surfaces [1]. DFT calculation also suggests that the activation barrier can be overcome by supplying energy to CO_2 molecules [2]. In this work, we conduct formate synthesis with transnationally and vibrationally hot CO_2 molecules to prove the mechanism of formate synthesis on Cu surfaces.

The translational and vibrational energy of CO_2 molecules is controlled by the supersonic molecular beam technic. Firstly hydrogen atoms are pre-adsorbed on Cu single crystal with hot tungsten filament. Then CO_2 molecular beam is irradiated to H/Cu surface. The relation between the energy of incident CO_2 molecules and the formation of formate are investigated using temperature programmed desorption and infrared reflection absorption spectroscopy.

[1] H. Nakano, I. Nakamura, T. Fujitani, and J. Nakamura, *J. Phys. Chem. B* **2001**, 105, 1355

[2] G. Wang, Y. Morikawa, T. Matsumoto, and J. Nakamura, *J. Phys. Chem. B* **2006**, 110, 9

SS-TuP9 Chemical and Electronic Structure of $(Y_{1-x}Ca_x)CrO_3$, $(0.00 \le x \le 0.15)$ in Core Levels and Valence Band by XPS and DOS, ***Lazaro Huerta***, *R. Escamilla, M. Cruz, A. Duran*, Universidad Nacional Autónoma de México

Polycrystalline samples of (Y1-xCax)CrO3 with $0.00 \le x \le 0.15$ were synthesized by combustion method. The samples were studied by X-ray diffraction (XRD) and photoelectron spectroscopy (XPS). Results of refinement of Rietveld shows that the cell volume decrease occurs through the change from Cr(III) to Cr(IV) as a result of the charge compensation of the Ca doping. XPS was used to investigate the binding energies of the Y 3d, Cr 2p, Ca 2p, and O 1s core level and Y 4d, Cr, 3d Ca 3d and O 2s contributions of valence band. The valence band measurement is consistent with the calculations of the band structure calculated near the Fermi level.

SS-TuP10 Wettability of MgO-P_2O_5 Glasses: Relation between Bulk and Surface Properties, ***Naoya Yoshida***, *N. Masuda, M. Yamada, T. Okura*, Kogakuin University, Japan

MgO-P_2O_5 glass system shows anomalous changes in bulk properties, such as density, with changing in its composition; density does not simply

increase with increase of MgO composition, and significantly decreases at around meta composition (50MgO-50P_2O_5). This phosphorus oxide anomalies derive from local structural changes between tetrametaphosphate and pyrophosphate structures.Wettability, one of the important surface properties, depends on surface energy and surface roughness, therefore, with samples of constant surface roughness, wettability simply reflects surface energy, which relates with chemical composition and structure of the surface.

Here, we prepared MgO-P_2O_5 glasses with changing composition from 35MgO-65P_2O_5 to 55MgO-45P_2O_5, and studied the relation between their bulk properties (density and solubility in water) and wettability. As a result, simple relation was found among wettability, density, and

solubility in water. Of course, wettability is only a surface phenomenon, however, the results suggested that bulk properties are possibly estimated by measurements of wettability. We will discuss the results of other glass systems such as Na_2O-B_2O_3.

SS-TuP11 Preparation and Characterization of Photocatalytic Thin Films of Zn-doped Calcium Phosphate, ***Yuji Nakamura***, *N. Yoshida, T. Okura*, Kogakuin University, Japan

Ti-doped hydroxyapatite (TiHAP), partially substituted Ca^{2+} with Ti^{4+}, exhibits photocatalytic activities such as decomposition of organic compounds similar to that of TiO_2, as our group has reported. Oxidation power of TiHAP seems to be weaker than that of TiO_2, and, it shows excellent adsorption ability derived from hydroxyapatite structure. The mechanism of phtocatalytic activities of TiHAP is still unknown, however, Ti-doping and/or defects derived from Ti-doping are thought to play an important role in photocatalytic reactions. Here, we tried to fabricate thin films of Zn-doped calcium phosphate, and to evaluate those photocatalytic activities.

Transparent and homogeneous thin films of Zn-doped calcium phosphate were successfully fabricated from a solution of zinc nitrate, calcium nitrate, and phosphorus oxide by spin-coating on glass substrates and following calcination. Several characterizations, such as UV-vis transmission and reflection spectroscopy, X-ray diffraction analysis, and surface structural analysis by atomic force microscope, were carried out. Methylene blue decomposition tests under irradiation of UV light suggested that photocatalytic activity was improved by Zn-doping.

SS-TuP12 Critical Review and Recommended Values of Work Functions for Low Index Faces of Clean Metal Surfaces, ***Gregory Derry***, Loyola University Maryland

Despite the fundamental interest and technological importance of the work function, the standard reference tables of this quantity used by the surface science community are outdated, incomplete, and include flawed experimental information. In this work, a thorough critical review of the entire literature is undertaken, with both the cleanliness and characterization of the surfaces and the reliability of the experimental techniques examined. Unreliable data is rejected and realistic uncertainty estimates are made for the all of the comparatively reliable data. Based on this information, recommended values of the work functions and their uncertainties are presented for all clean metal surfaces with low index crystal faces for which good data exists, along with updated tables that include all of the primary references and relevant information needed to evaluate each surface and generate such recommended values. Details of the evaluation protocols employed are also presented. It is anticipated that the information presented here will be useful both in technological applications (such as electrochemistry and microelectronics) and in the testing of theoretical models for electrons at metal surfaces.

SS-TuP13 Unveiling Hidden Information in Temperature-Programmed Desorption-Reaction Data: Identification of Desorbing Compounds by Their Desorption and Fragmentation Patterns, ***JuanCarlos Rodríguez-Reyes***, Universidad de Ingeniería y Tecnología, UTEC, Peru, *J.-M. Lin, J. Zhao, A.V. Teplyakov*, University of Delaware

Temperature-programmed desorption/reaction (TPD/R) experiments are very powerful for providing information in several fields related to surface science, including heterogeneous catalysis, thin film precursor analysis and thermal treatments. Data can be, however, very complex and difficult to extract, especially when competing reaction pathways yield products with similar spectrometric features. We present a mathematical method for analyzing TPD/R data, which is able to extract, for each desorbing compound, its desorption pattern and its fragmentation pattern. This methods is called multivariate curve resolution (MCR) and, briefly, requires the organization of data (e.g. "n" m/z traces followed over "t" temperature points) as a (n x t) matrix, which can be seen as the product of two matrices, (n x k) and (k x t), where k is calculated by considering variations and correlations between m/z traces. Interestingly, k turns out to be the number of components (compounds desorbing from a surface), and its value is limited not only by correlations between data points, but also by the fact that intensities in the two matrices cannot be negative. Therefore the two matrices correspond to the fragmentation pattern, (n x k) matrix, and to the desorption pattern, (k x t) matrix. Since it is a mathematical method, MCR is applicable even when no previous knowledge of the system under investigation is available. However, any available information can be used as constraints that guide the outcome, increasing the accuracy of the resolution. The usefulness of this method is demonstrated using datasets from a variety of surface reactions, including the reaction of ethyl halides with a Si(100) surface and the thermal decomposition of the TiN precursor tetrakisdimethylamido titanium, TDMAT.

SS-TuP14 Dependence on an O_2 Gas Flow Rate of NiO Thin Films 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. Silicon-based solar cells having over 30% in the theoretical efficiency are the present mainstream, however the single crystal-silicon has a problem on the manufacturing cost. Further more the high purity silicon that is the main raw material for solar cells is insufficient worldwide, and so a new solar cell without silicon that is replaced silicon-based solar cells has been required. Practical application of oxide-based thin film solar cells is expected in reduction of energy costs or environmental loads.

Generally a typical oxide-based thin film solar cell is a wet dye-sensitized solar cell composed of an electrolyte, an electrode of 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 problem was Cu diffusion from underlayer Cu_2O. The diffusion of Cu induced collapse of p-n junction. In this study, we used NiO as a next p-type oxide semiconductor instead of Cu_2O. The NiO thin film is used as the transparent oxide semiconductor. Most of the transparent oxide semiconductors are an n-type semiconductor, while NiO is a p-type semiconductor. The NiO thin films prepared by changing an oxygen gas flow rate were evaluated by crystallinity, optical properties, semiconductor properties, surface morphology in comparison with Cu_2O thin films.

NiO thin films were fabricated by reactive magnetron sputtering. As substrates, the glass (Corning#1737) and ITO-film coated glass were ultrasonically cleaned. The NiO thin film was deposited on those substrates 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 changed at 2.0 sccm, 2.7 sccm, 3.2 sccm, 3.7 sccm and 4.4 sccm. A thickness of the NiO thin films was kept at about 200 nm.

The NiO thin films were successfully fabricated by reactive magnetron sputtering. The XRD pattern of the NiO thin film showed the stronger peak at the (012) crystal plane of NiO, when the flow rate of an oxygen gas was lower. The resistivity of NiO thin films showed a higher value than that of Cu_2O thin film and the mobility of NiO thin films showed a lower value than Cu_2O.

SS-TuP15 Properties of Cu/Ti Thin Films on the Biodegradable Resin Irradiated by an Ar^+ Ion Beam, ***Ryosuke Tan***, *I. Takano*, Kogakuin University, Japan

Recently, biodegradable resin attracts attention as one of the effective use of resources on environmental measures. PGA (Polyglycolic acid) used in this study is categorized to a kind of polyester resin and is composed of hydrogen, carbon and oxygen. PGA shows a high gas barrier property, a high hydrolysis property and high mechanical strength. These characteristics are applied for sutures of surgery or multi-layer PET bottles, while there is hardly application in an electronic field. The usage of PGA in electronic parts such as a printed circuit board has the important role in environmental measures, however there are some problems that have to be overcome.

In this study, the surface of PGA was modified by using an ion beam so that the durability of the PGA coated with metal films was improved. The ion beam cut off the bonding of molecules and as a result the surface of PGA turned to a carbon layer which was stable against heating or humidity. Double layer films of Cu/Ti were deposited on the modified PGA by vacuum evaporation. The Ti layer between the Cu film and the modified PGA (carbon layer) improved adhesion and electrical conductivity. The ion beam irradiation and vacuum evaporation were performed using the high current ion implanter with an electron beam evaporator. The ion beam was extracted from the bucket- type ion source with multi-aperture electrodes of 100 mm in diameter.

The Ar^+ ion irradiation conditions were controlled at a current density of 20 $\mu A/cm^2$, an acceleration voltage of 1 kV and irradiation time of 50 s. The deposition conditions of Ti were kept at a deposition rate of 0.3 nm/s and were changed a film thickness of 0-200 nm. The deposition conditions of Cu were kept at a deposition rate of 0.3 nm/s and a film thickness of 200 nm. The kind of prepared samples was the metal coated PGA sample, the ion irradiated PGA sample and the metal coated sample on the irradiated PGA. The sample hardness was measured by a load-unloading method using a micro-hardness tester with a Knoop indenter. Electrical conductivity of metal films was calculated from V-I characteristics measured using the four probe method. A surface chemical-bonding state was investigated by X-ray photoelectron spectroscopy.

The Ti layer between the Cu film and the carbon layer improved adhesion and electrical conductivity of samples. Those properties showed the maximum value at 50 nm in a Ti thickness, while the excess Ti-layer thickness decreased those properties. The measurement results of electrical conductivity suggested the possibility of PGA used as a printed circuit board.

SS-TuP17 Understanding the Growth and Activity of Monometallic and Bimetallic Clusters on $TiO_2(110)$, ***Randima Galhenage****, University of South Carolina, *H. Yan*, Brookhaven National Laboratory, *D.A. Chen*, University of South Carolina

The study of metal clusters on single-crystal oxide supports has garnered much attention as model systems for fundamental investigations of surface activity that can guide the rational design of new catalyst. We have studied the growth and activity of monometallic and bimetallic clusters on $TiO_2(110)$ for metals such as Au, Co, Pt and Re, since these metals are known to have desirable properties for alcohol reforming and oxidation reactions. Scanning tunneling microscopy studies show that the cluster size and number of nucleation sites for these metals depend on the mobility of each metal on the titania surface. In general, the diffusion length decreases with increasing metal-titania bond strengths, and DFT studies show that the metal-titania bond strengths can be predicted directly from metal-oxygen bond strengths. Bimetallic clusters (Au-Co, Pt-Co, Pt-Re) were prepared from sequential deposition by growing the metal with the lower mobility first, followed by the more mobile metal. In general, exclusively bimetallic clusters are formed when the number of seed clusters generated from the deposition of the first metal provides a sufficient number of nucleation sites for the second metal. Surface compositions for the clusters were investigated by low energy ion scattering spectroscopy; for metals that do not alloy in the bulk, like Co and Au, core-shell structures are formed, and the surface composition is determined by the relative surface free energies. For metals that are bulk miscible, like Co-Pt and Pt-Re, both metals exist at the surface, regardless of the relative surface free energies. The chemical activity of the bimetallic clusters for CO adsorption and methanol reaction were investigated by temperature programmed desorption experiments. The addition of Au and Pt to Co clusters increased the thermal stability of the surface intermediate by inhibiting C-H bond scission and resulted in H_2 and CO desorption at higher temperatures.

SS-TuP18 Conductivity of Graphene as a Function of its Lattice Orientation Relative to Substrate Layers, ***Hyunsoo Lee†***, KAIST, Republic of Korea, *Y. Qi*, Okinawa Institute of Science and Technology Graduate University, Japan, *S. Kwon*, KAIST, Republic of Korea, *M.B. Salmeron*, Lawrence Berkeley National Laboratory, *J.Y. Park*, KAIST, Republic of Korea

We report strongly varying electrical transport properties of graphene layers on graphite that depend on the relative lattice orientation of the surface and subsurface layers. Employing the pressure dependence of conductance on the surface of highly ordered pyrolytic graphene (HOPG) using the conductive tip of an atomic force microscope as an electrode, we found that the electrical conductivity of graphite terraces separated by steps can vary by large factors of up to 100. This effect can be attributed to interlayer interactions when stacked commensurately in a Bernal sequence (ABAB…), which opens a band gap, while rotational misaligned layers behave as graphene. Small angular misorientations of a few degrees were found to give rise to large increases in the conductivity of the top layer, with the maximum occurring at around 30°. In addition, two types of steps were encountered on HOPG surface: external steps where the edge C atoms have dangling or broken bonds, and internal steps where the bonds are only broken in the second layer or deeper. Accordingly, graphite layers covering several underlying terraces and steps retain the same conductivity across the terraces. Top layer terraces have higher friction on the edges, making it easy to distinguish them from subsurface steps where no friction changes occur. These results suggest new applications for graphene multilayers using stacked layers at various angles to control the resistance of connected graphene ribbons in devices.

SS-TuP19 Electron Percolation via In-Gap States in Semiconductor Quantum Dot Arrays, ***Yingjie Zhang†***, University of California, Berkeley and Lawrence Berkeley National Laboratory (LBNL), *D. Zherebetskyy, S. Barja, L. Lichtenstein*, LBNL, *N.D. Bronstein*, University of California, Berkeley, *P. Alivisatos*, University of California, Berkeley and LBNL, *L.-W. Wang*, LBNL, *M.B. Salmeron*, University of California, Berkeley and LBNL

Charge hopping and percolation in disordered semiconductors has been widely studied, but the microscopic nature of the percolation process is not understood and has never been determined. Here we directly image the charge percolation pathways in 2-D PbS quantum dot (QD) arrays using Kelvin probe force microscopy. We showed that the electrons percolate via in-gap states (IGS) instead of the conduction band, while holes percolate via valence band states. This exotic transport behavior is explained by the electronic structure and energy level alignment of the individual QDs, which was measured by scanning tunneling spectroscopy. Density functional theory and spectroscopic analysis show that the IGS are induced by oxygen molecules adsorbed on the QDs' surface. These states are partially hybridized with the valence band states, enabling inter-IGS coupling and electron transport via IGS. Surface chemical treatments open the way of defect engineering, achieving tunable electronic structure and transport properties by controlling the IGS.

SS-TuP20 Mechanisms of CO Oxidation on Well-defined Pd Oxide Films on Pd(111), ***Feng Zhang†***, *T. Li*, University of Florida, *L. Pan, A. Asthagiri*, The Ohio State University, *J.F. Weaver*, University of Florida

The surface chemistry of late transition-metal oxides has attracted significant attention due largely to observations that the formation of metal oxide layers can drastically alter the catalytic performance of parent metals in applications of oxidation catalysis. For example, previous *in situ* studies have shown that CO oxidation over palladium undergoes a significant rate increase when the palladium surface becomes oxygen rich. This observation has been attributed to the formation of various types of palladium oxide layers or surface oxygen phases, though the reaction mechanisms have not been determined in detail. In this presentation, I will show results of recent experiments and density functional theory (DFT) calculations in which we studied CO oxidation on well-defined Pd oxide surfaces. In the experiments, we utilized mass spectrometry to investigate the CO oxidation kinetics on both surface and bulk Pd oxides during TPRS and under isothermal conditions and used reflection absorption infrared spectroscopy

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*** Morton S. Traum Award Finalist**

(RAIRS) to monitor the evolution of CO binding states and hence the formation of new surface phases as the oxides undergo reduction.

In direct rate measurements under isothermal condition, we find that the initial reaction rates are nearly ten times larger on PdO(101) compared with the Pd_5O_4 surface oxide, demonstrating that PdO(101) has a much higher intrinsic activity toward CO oxidation compared with the surface oxide. The measurements also show that the reactions occur on both oxide surfaces in an autocatalytic fashion, where the CO_2 generation rate increases as oxygen on the surface is consumed. The RAIRS data shows that the reduction of PdO(101) by CO initially creates oxygen vacancies and that CO preferentially binds to atop-Pd sites located next to the O-vacancies. This atop CO-species yields a characteristic IR peak between 2090 cm^{-1} and 2060 cm^{-1}. DFT results agree very well with the measured C-O stretching frequencies, and further show that CO achieves significantly stronger binding on an atop-Pd site located next to an oxygen vacancy vs. on the pristine PdO(101) surface. In addition to oxygen vacancies, we also find that surface metal domains develop during the early stages of isothermal reaction of CO on PdO(101) and the Pd_5O_4 surface oxide, except that on the Pd_5O_4 surface CO reaction only leads to the creation of metallic domains without producing oxygen vacancies. Thus, the autocatalytic kinetic behavior observed for both oxides arises from a similar mechanism wherein surface reduction during CO oxidation continually creates sites that bind CO strongly and thus facilitate the adsorption and subsequent reaction of CO.

SS-TuP21 Surface Structure and Chemistry of Rh(110) Model Catalyst under Reaction Condition and during CO Oxidation, *Luan Nguyen**, *L. Liu, S. Zeng, F. Tao*, University of Notre Dame

Heterogeneous catalysis is a chemical process performed at a solid/gas or solid/liquid interface. An elevated pressure of a reactive environment could cause materials surface likely to restructure geometrically and electronically to adapt to the surroundings. Since catalytic performance (activity, selectivity, promotion effect, deactivation, etc.) depends on the surface structure of a catalyst during the reaction, it is necessary to study the surface under reaction condition (a reactant) and during catalysis (a mixture of all reactants).

Since a high pressure of a reactant gas typically results in high adsorbate coverage, one alternative approach to mimic the gas environment of a high pressure is to increase coverage of absorbate by lowering the catalyst temperature. However, decreasing of catalyst temperature in low pressure environment is only valid when entropy effects are negligible and the relevant adsorption structure is not kinetically hindered. In fact, the magnitudes of entropy contribution to the surface free energy in ultrahigh vacuum (UHV) and under an ambient pressure of a reactant gas are actually different by about 0.3 eV or even larger. Therefore, pressure-dependent entropy can lead to large restructuring of catalyst surfaces. It is difficult to predict how a system will respond to the change of pressures of gases and temperatures of catalysts. Here we will present an in-situ investigation of a model catalyst surface Rh(110) which revealed interesting restructuring of Rh(110) surface in pure CO and a mixture of CO and O_2 in the temperature range of 25ºC-130ºC.

In UHV environment clean Rh(110) surface exhibits a (1x1) structure. However, upon O_2 adsorption at elevated temperature (approximately 500 °C), the surface reconstructs to an O-covered (1x2) missing row structure, namely Rh(110) (2x2)p2mg-O. High pressure STM and ambient pressure XPS were used in in-situ studies of surface chemistry and structure of Rh(110) in the mixture of CO and O_2. . Initially, the Rh surface exhibits a (1x2) missing row structure. During CO (0.08 Torr) oxidation with O_2 (0.02 Torr) at room temperature, the (1x2) structure reconstructs to form (1x1) islands. Interestingly, no surface reconstruction was observed when Rh(110)-(2x2)p2mg-O surface was exposed to only one reactant gas, CO or O_2 at room temperature, or in the mixture of CO and O2 at in the pressure range of 10^{-7} Torr. The surface chemistry and structure of Rh(110) in pure CO, O_2 and mixture of CO and O_2 at different temperatures and pressures will be presented. A correlation between surface chemistry and structure of this catalyst during CO oxidation and its catalytic activity will be discussed.

SS-TuP22 Mechansim of Formation of Zinc Oxide Nanostructures Synthesized by Photon Irradiation, *Rupali Nagar*, Symbiosis Institute of Technology (SIT), Symbiosis International University (SIU), India, *A. Praveen, S. Ramaprabhu*, Indian Institute of Technology Madras, India

Zinc oxide (ZnO) is a wide bandgap semiconductor with strong room temperature luminescence, high electron mobility and good transparency. These properties make it an attractive transparent conducting oxide rendering it suitable for optical and photovoltaic applications. It is imperative to devise synthesis techniques that are quick, safe, economical, and easy to implement. In this direction, ZnO nanostructures were synthesized by photon irradiation technique by using different sets of precursors and reducing agents. The synthesized nanostructures were characterized by X-ray diffraction, scanning and transmission electron microscopy, and optical properties investigated by UV-Visible and Raman spectroscopy. Various aspects of the synthesis procedure are compared to understand the mechanism of formation of nanostructures, and the effects of pH, irradiation time that impact the morphology and yield of ZnO nanostructures are discussed.

SS-TuP23 Crystallization and Phase Separation Kinetics of Organic Molecules from Solution on Si(111) Substrates, *Miriam Cezza*, *R.J. Phaneuf*, University of Maryland, College Park

Understanding the underlying science behind the arrangements of small organic molecules in mixtures is important for numerous technological applications, among which organic solar cells (OSCs) are especially noteworthy, given the drive toward alternative energy sources. An important process on which organic solar cells depend is the phase separation of organic small molecules. The spontaneous formation of a particular morphology during phase separation from a solvent-based, bimolecular solution onto a substrate depends on several parameters, including relative molecular concentrations, solubilities of each type of molecule in the solvent, mutual interaction between molecules of the same species, interaction of individual molecules with the substrate surface, solvent evaporation rate, and annealing conditions. In this work, we carry out a study of molecular mixtures consisting of tetranitro zinc-phthalocyanine (tn-ZnPc) and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) using chloroform as a solvent, and native oxide-covered Si(111) substrates. We investigate the role that the solvent evaporation rate during deposition, followed by solvent vapor annealing (SVA), plays on the formation of phase separated mixtures and their crystallization and phase transformation. We also investigated the relative concentration of individual molecules in the mixtures. We found that the PCBM molecules alone undergo several phase transformations as the evaporation rate of the solvent decreases and upon SVA, while the tn-ZnPc molecules alone are very stable. Moreover, the concentration of the phthalocyanine molecules in the mixture with the PCBM highly affects the crystallization process of the latter.

*** Morton S. Traum Award Finalist**

2D Materials Focus Topic
Room: 310 - Session 2D+EM+NS+SS+TF-WeM

Novel 2D Materials
Moderator: Evan Reed, Stanford University

8:00am **2D+EM+NS+SS+TF-WeM1 Silicene and Germanene: Novel Graphene-like Artificial Silicon and Germanium Allotropes**, ***Guy Le Lay***, Aix-Marseille University, France **INVITED**

Silicene, graphene's cousin, and germanene, a new born in Terra Plana, are predicted to combine the unique electronic properties of graphene associated to quasiparticles behaving as massless Dirac fermions to a character of two-dimensional topological insulators, and, even, possibly, high temperature superconductors. In this talk, I will present fundamental results on these novel synthetic 2D materials, which do not exist in nature, but which might open the way to practical applications, because of their expected direct compatibility with the current nano/micro electronic technologies.

8:40am **2D+EM+NS+SS+TF-WeM3 Silicon Growth at the Two-Dimensional Limit on Ag(111)**, ***Andrew Mannix***, *B.T. Kiraly,* Northwestern University*, B.L. Fisher,* Argonne National Laboratory*, M.C. Hersam,* Northwestern University*, N.P. Guisinger*, Argonne National Laboratory

Bulk silicon has played a dominant role in the growth of microelectronics over the past 50 years. Considering the immense interest in two-dimensional (2D) materials (e.g., graphene, MoS_2, phosphorene, etc.), the growth of Si in the 2D limit is of high relevance to the evolution of electronic materials. Utilizing atomic-scale, ultra-high vacuum (UHV) scanning tunneling microscopy (STM), we have investigated the 2D limits of Si growth on Ag(111). In agreement with previous reports of sp^2-bonded silicene,[1,2] we observe the evolution of ordered 2D phases, which we attribute to apparent Ag-Si surface alloys. At sufficiently high Si coverage, we observe the precipitation of crystalline, sp^3-bonded Si(111) domains. These domains are capped with a $\sqrt{3}$ honeycomb phase that is indistinguishable from the $\sqrt{3}$ honeycomb-chained-trimer (HCT) reconstruction of Ag on Si(111).[3,4,5] Additional evidence suggests that silicon intermixing with the Ag(111) substrate is followed by the precipitation of crystalline, sp^3-bonded silicon nanosheets. These conclusions are supported by *ex-situ* atomic force microscopy (AFM), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). Even at the 2D limit, scanning tunneling spectroscopy shows that the sp^3-bonded silicon nanosheets exhibit semiconducting electronic characteristics.

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[5] Ding, Y., Chan, C., & Ho, K. Structure of the $(\sqrt{3}\times\sqrt{3})$ R30° Ag/Si (111) surface from first-principles calculations. *Phys. Rev. Lett.*, *67*(11), 1454–1458 (1991).

9:00am **2D+EM+NS+SS+TF-WeM4 Growth, Structure, and Properties of 2D SiO_2 Polymorphs**, ***Eric Altman***, *J. Götzen, X. Zhu, A. Sonnenfeld, U.D. Schwarz*, Yale University

Recently it has been shown that SiO_2 can form closed 2D bilayers; because the layers have no dangling bonds they are expected to interact solely through van der Waals interactions. Despite the expected weak interactions, hexagonal crystalline bilayers on Pd(100) are stretched 4% to match the lattice constant of the substrate. Both electron diffraction and STM reveal that the size of the crystalline domains is limited along Pd[011] and one of the other bilayer close-packed directions but was long along the third one. The formation of regular domain boundaries on the square Pd substrate is attributed to stress relief in the crystalline layer. Ab initio calculations indicate that much of the remaining strain energy can be relieved by allowing the film to relax along the incommensurate direction. In this way the square substrate actually aids the templating of the overlayer despite the severe geometric mismatch. The calculations also indicate that the bilayer is surprisingly compliant, explaining the lattice matching despite the weak interaction and poor match. Amorphous bilayers could also be prepared on Pd(100). Atomic-scale features in STM images of the amorphous film could be associated with 4-9 membered rings of corner-sharing SiO_4 tetrahedra. In addition to the structural heterogeneity, spectroscopic STM imaging revealed electronic heterogeneity with oxygen sites joining larger rings of corner-sharing SiO_4 tetrahedra fading at low bias; spectra revealed two distinct electronic states responsible for this phenomenon. MBE growth of silica bilayers on graphene layers grown on epitaxial Ru on sapphire will also be discussed.

9:20am **2D+EM+NS+SS+TF-WeM5 Layer-dependent Electronic and Vibrational Properties of $SnSe_2$ and SnS_2 2D Materials***,* ***Joseph Gonzales***, *R. Schlaf, I.I. Oleynik*, University of South Florida

Layered metal chalcogenides possess a wide range of unique electronic properties, which are currently explored for applications as novel two-dimensional electronic materials. SnS_2 and $SnSe_2$ layered materials consist of covalently bonded S-Sn-S (Se-Sn-Se) sheets bonded together by weak van der Waals interactions. The atomic, electronic and vibrational properties of SnS_2 and $SnSe_2$ thin films are investigated using first-principles density functional theory (DFT). The accurate prediction of electronic and optical properties of SnS_2 and $SnSe_2$ layered 2D materials is achieved by applying state of the art many-body perturbation theory in GW approximation followed by solving the Bethe-Salpeter equation (BSE) to take into account excitonic effects. The evolution of the thickness-dependent band structure, optical and Raman spectra are discussed. The strain effects due to interactions with the substrate are also considered. The first-principles results are compared with available experimental data.

9:40am **2D+EM+NS+SS+TF-WeM6 Synthesis and Properties of Large Scale, Atomically Thin Tungsten Diselenide (WSe_2)**, ***Sarah Eichfeld***, *Y.C. Lin, L. Hossain,* The Pennsylvania State University*, A. Piasecki,* The Pennsyvania State University*, A. Azcati,* University of Texas, Dallas*, S. McDonnell, R.M. Wallace,* University of Texas at Dallas*, J.A. Robinson*, The Pennsyvania State University

Transition metal dichalcogenides (TMDs), such as tungsten diselenide (WSe_2) are of interest due to their intriguing properties including the transition from indirect gap to direct gap as the material is thinned to a single atomic layer. Stacking of these layered TMDs also allows for the possibility of bandgap tuning. These properties can suit a large range of flexible and low temperature electronic and optoelectronic devices. Current methods of WSe_2 research involve exfoliation or vaporization of WO_3 and Se powder, which limits industrial scalability. This work is focused on development of a metal-organic chemical vapor deposition process that can controllably produce highly-crystalline, atomically thin WSe_2 on large area substrates.

Growth of controlled monolayer tungsten diselenide (WSe_2) was carried out using chemical vapor deposition in a cold wall vertical reactor. Tungsten hexacarbonyl ($W(CO)_6$) and dimethylselenium (DMSe) served as the tungsten and selenium precursors, respectively. Use of MOCVD precursors provides a means to independently control the W and Se precursors allowing for more precise control of the individual species during growth. Process variables including temperature (500-950°C), pressure (100-700 Torr), and carrier gas, which were correlated with grain size, growth rate, and nucleation density of the WSe_2 to identify optimal parameters for atomically controlled synthesis. Increasing the growth pressure from 100-700 Torr results in a decrease in growth rate and nucleation density, leading to a >50x increase in grain size. Increased growth temperatures yield an increase in grain size, however, it was found that above temperatures of 800 °C the sapphire substrate begins to decompose in the growth environment, resulting in a degradation of WSe_2 above 800°C. Synthesis using 100% hydrogen, and also hydrogen/nitrogen mixtures was carried out. It was found that 100% hydrogen was necessary in order to achieve low carbon incorporation in the WSe_2 films. Characterization of these samples via Raman and photoluminescence spectroscopy verified that high quality, monolayer WSe_2 is readily achievable. Additional characterization (i.e. scanning electron microscopy, atomic force microscopy, etc.) verify the quality, grain size, and nucleation density of the atomic layers. Finally, we will discuss the impact of substrate choice on the quality of the WSe_2 atomic layers, as well as providing direct evidence that synthesis on graphene results in highly textured films, with nearly 100% commensurability to the underlying graphene.

11:00am **2D+EM+NS+SS+TF-WeM10 Growth of Transition Metal Dichalcogenides and their Alloys and on Flat and Patterned Substrates**, *E. Preciado, A. Nguyen, D. Barroso, V. Klee, S. Bobek, I. Lu, S. Naghibi, G. Von Son Palacio, T. Empante, K. Brown, K. Yang, A. Nguyen, J. Mann,* ***Ludwig Bartels***, University of California - Riverside

The use of organic chalcogen precursors permits the CVD growth of $MoS_{2(1-x)}Se_{2x}$ alloys of any composition between pure MoS_2 and $MoSe_2$ on SiO_2. Spatially resolved vibrational and photoluminescence (PL) spectroscopy is used to characterize our samples: while we observe a continuous transition of the PL maximum with S: Se ratio, the vibrational modes behave in a more complicated, 2-mode fashion. Depending on growth conditions, compositional homogeneous and heterogeneous films can be prepared.

We present details of our growth processes and show to which extend patterns on the substrates can affect the resultant structures. The patterns range from simple hole and pillar arrays to complex waveguide structures. We find that holes to an underlying reducing substrate (silicon) are effective in seeding growth. In contrast, protrusions on the substrate have little effect, so that complex devices can be overgrown.

Ref: Mann et al., 2-Dimensional Transition Metal Dichalcogenides with Tunable Direct Band Gaps: $MoS_{2(1-x)}Se_{2x}$ Monolayers, Advanced Materials 26, 1399 (2014)

11:20am **2D+EM+NS+SS+TF-WeM11 Synthesis, Characterization and Radiation Response of Boro-Carbon-Oxy-Nitride: A Heterogeneous 2D Material**, ***GaneshRahul Bhimanapati***, *M. Wetherington, M. Kelly, J.A. Robinson*, The Pennsylvania State University

Since graphene, there have been many other two-dimensional materials systems (e.g., boron nitride (hBN), borocarbon nitride (BCN), transition-metal dichalcogenides) that provide an even wider array of unique chemistries and properties to explore future applications. In fact, these other 2D materials, are sometimes far better suited for many optoelectronic and mechanical applications. Specifically, tailoring graphene/boron nitride heterostructures, which retain the character of single-atom thick sheets that can withstand large physical strains, are easily functionalized, and have entirely different optical and mechanical properties compared to graphene can provide the foundation for entirely new research avenues. In recent years, it has been shown that because of the similar crystal structure, carbon, boron, and nitrogen can coexist as atomic sheets in a layered structure. Thus, combining these materials to form a new heterogeneous material system known as boro-carbon-oxy-nitride (BCON) for potential nano-mechanical and electronic applications and to study its fundamental property relations is necessary. Here, we present the fundamental property relations of BCON and its structural response to various radiation sources such as alpha, beta and gamma particles thereby providing a means for potential radiation sensing applications.

We have developed a facile method of integrating boron nitride and graphene oxide (GO) via chemical exfoliation. Chemical exfoliation of graphene oxide and boron nitride powders is accomplished via oxidation in strong acids, as we find previous methods of sonication in polar solvents does not yield stable solutions of hBN .Upon exfoliation, GO and hBN are mixed, and the resulting BCON material can be suspended in DI water, with suspension stability depending on the pH of the GO. The study of the stability of this material at different pH conditions indicates a stable and a uniform solution is achievable at pH 4-7. Fourier transform infrared spectroscopy (FTIR) indicates the B-N-B bending in the BCON is decreased as an effect of parent GO. Further, radiation response of this material to various radiation sources such as alpha, beta and gamma radiation are studied using In-Situ X-Ray Photoelectron Spectroscopy (XPS). The structural changes of carbon 1s peak in the BCON even for very low doses of radiation energy indicate potential applications in radiation sensing.

11:40am **2D+EM+NS+SS+TF-WeM12 The Structure of 2D Glass**, ***Christin Büchner***, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, *L. Lichtenstein,* Lawrence Berkeley National Laboratory, *M. Heyde, H.-J. Freund*, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany **INVITED**

For the first time, the structure of an amorphous network is imaged in real space.[1] Through a thin film approach, silica is made accessible for investigation with scanning tunneling microscopy (STM) and atomic force microscopy (AFM). Physical vapor deposition with subsequent annealing is employed to create an atomically flat bilayer of SiO_2, supported on a Ru(0001) single crystal. Atomic positions of oxygen and silicon can be visualized, as well as ring structures with their distributions and local neighborhoods. All atomic species on the surface can be directly assigned with chemical sensitivity imaging.[2] This allows for statistical analysis of the building units, comparing amorphous to crystalline regions, as well as experiment to theory. Pair correlation functions of the 2D film structure are set against diffraction data of bulk silica, revealing very similar bond distributions.

Coexisting crystalline and amorphous areas allow imaging of a topological transition region.[3] The understanding of glassy structures gained from these experiments is the starting point for more in-depth structural investigations[4], but also for investigating thin films with modified composition. Al-doping or Fe-doping can be employed to create 2D-Aluminosilicates or 2D-Clays, respectively.[5] Adsorption properties of the film can be probed using single metal atoms which migrate through the film, exhibiting ring-size-selectivity.[6]

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In-Situ Spectroscopy and Microscopy Focus Topic
Room: 313 - Session IS+AS+MC+SS-WeM

In-Situ X-ray Absorption and Raman Spectroscopy
Moderator: Hirohito Ogasawara, SLAC National Accelerator Laboratory

8:00am **IS+AS+MC+SS-WeM1 *In Situ* Studies on the Behavior of Metal/Oxide Catalysts during the Water-gas Shift Reaction**, ***Jose Rodriguez***, *D. Stacchiola, S. Senanayake, J. Hanson*, Brookhaven National Laboratory **INVITED**

In this talk, it will be shown how a series of *in-situ* techniques [X-ray diffraction (XRD), pair-distribution-function analysis (PDF), X-ray absorption spectroscopy (XAS), environmental scanning tunneling microscopy (ESTM), infrared spectroscopy (IR), ambient-pressure X-ray photoelectron spectroscopy (AP-XPS)] can be combined to perform detailed studies of the structural, electronic and chemical properties of metal/oxide catalysts used for the production of hydrogen through the water-gas shift reaction (WGS, $CO + H_2O \rightarrow H_2 + CO_2$). Under reaction conditions most WGS catalysts undergo chemical transformations that drastically modify their composition with respect to that obtained during the synthesis process. The active phase of catalysts which combine Cu, Au or Pt with oxides such as ZnO, CeO_2, TiO_2, CeO_x/TiO_2 and Fe_2O_3 essentially involves nanoparticles of the reduced noble metals. The oxide support undergoes partial reduction and is not a simple spectator, facilitating the dissociation of water and in some cases modifying the chemical properties of the supported metal. Therefore, to optimize the performance of these catalysts one must take into consideration the properties of the metal and oxide phases. IR and AP-XPS have been used to study the reaction mechanism for the WGS on the metal/oxide catalysts. Data of IR spectroscopy indicate that formate species are not necessarily involved in the main reaction path for the water-gas shift on Cu-, Au- and Pt-based catalysts. Thus, a pure redox mechanism or associative mechanisms that involve either carbonate-like (CO_3, HCO_3) or carboxyl (HOCO) species should be considered. In the last two decades, there have been tremendous advances in our ability to study catalytic materials under reaction conditions and we are moving towards the major goal of fully understanding how the active sites for the production of hydrogen through the WGS actually work.

8:40am **IS+AS+MC+SS-WeM3 Tuning Catalytic Performance of Bimetallic Nanoparticle Catalysts through a Single or Sequential Post-Synthesis Reaction in a Gas Phase**, *F. Tao, J. Shan, S. Zhang, L.T. Nguyen,* University of Notre Dame, *A. Frenkel,* Yeshiva University, *J. Greeley,* Purdue University, ***Shibi Zeng***, University of Notre Dame

Besides a sophisticated synthesis of bimetallic nanocatalysts in a colloidal solution, a post-synthesis reaction in a gaseous phase is a complementary method to tailor the surface structure and composition of a bimetallic nanocatalyst to tune its catalytic performance. Here we illustrate the capability of creating a new catalyst surface exhibiting a lower activation barrier through segregation of a bimetallic catalyst in a post-synthesis reaction in a reactive gaseous environment. In-situ surface chemistry of bimetallic nanocatalysts were analyzed with AP-XPS. Coordination environment of Pt and Cu atoms under different reaction conditions was tracked with in-situ EXAFS. The surface restructuring was simulated with DFT calculation from thermodynamic,ci point of view. The composition and geometric structure of the newly formed surface of the bimetallic nanocatalysts strongly depend on the reactant gas used in the post-synthesis reaction. A further sequential reaction in a different gas after the initial post-synthesis reaction in a gas forms a different catalyst surface. A post-synthesis reaction of a Pt-Cu regular nanocube (Pt-Cu RNC) in hydrogen forms a near surface alloy (NSA) which exhibits an activation barrier of 39 kJ/mol for CO oxidation, much lower than pure Pt nanocubes. These studies demonstrate a method of tuning catalytic performances and generate another catalytic phase through a post-synthesis reaction in a gas phase.

9:00am **IS+AS+MC+SS-WeM4** ***In Situ* Characterization of Metal-Based Ionic Liquids using X-ray Spectroscopy**, ***Robert Meulenberg***, University of Maine, *C. Apblett, H. Pratt, T. Anderson*, Sandia National Laboratories

Energy storage for vehicles is advancing rapidly, and one of the possible contenders for a battery that can quickly be recharged is a redox flow battery, which uses liquids that are pumped into the battery to be charged or discharged, and then removed to storage containers. This makes the chemistry roughly analogous to liquid fuels employment, where the charged chemistry is pumped into the battery, discharged, and then pumped into a waste container, similar to fuel pumped into an engine, ignited, and then expelled through the tailpipe. Unlike internal combustion engines, however, the discharged product is retained on the vehicle, and can be subsequently either recharged on the vehicle, or pumped off the vehicle to be recharged at a filling station, while replacing with freshly charged material.

To date, however, the concentrations of most redox flow battery chemistries have been low, below the 1-2M concentration level. Recently, a new type of ionic liquid (IL) redox flow chemistry has been developed that raises this to 5-6M, and improves the energy density of the system. However, little is known about the structure of the molecule in the charged and discharged states. The current understanding of the structure of the IL, primarily the Fe IL, comes from primarily from FTIR, Raman, and TGA/DSC data, as traditional methods such as NMR to probe surface chemistry are limited due to the paramagnetic Fe center. It is believed the coordination of the ligand to the metal center occurs primarily through the alcohol groups. Cyclic voltammetry of the FeIL exhibits behavior associated with Fe(III)/Fe(II) reduction/oxidation, with some evidence that the ligands are coordinating to adjacent Fe atoms, resulting in antiferromagnetic coupling between the metal centers. A complete, fundamental understanding of the local coordination and ligand environment is not known and is the primary goal of our research. To further understand this structure, we have constructed a new electrochemical cell to be used for *in situ* transmission Fe K-edge x-ray absorption fine structure (XAFS) spectroscopy. We conduct our measurements at various states of charge, and the structure of the molecule in these various states is determined using this from analyzing both the XANES and EXAFS. Effects of electrochemical cell potential on local structure of the FeIL will be discussed.

9:20am **IS+AS+MC+SS-WeM5 Monitoring Catalysts during Catalytic Reactions with *In Situ* Raman Spectroscopy**, ***Israel Wachs***, Lehigh University **INVITED**

The surfaces of heterogeneous catalysts in reactive environments are dynamic and require *in situ* characterization studies under reaction conditions to fully understand their fundamental structure-activity relationships. This presentation will focus on the application of Raman spectroscopy to determine the nature of the catalytic active sites in different reaction environments. Emphasis will be placed on investigating heterogeneous supported metal oxide catalysts containing multiple catalytic active sites and determining the roles of each of the sites. Some of the examples to be presented will be the metathesis of $H_2C{=}CHCH_3$ to $H_2C{=}CH_2$ and $H_3C\text{-}CH{=}CHCH_3$ by supported ReO_x/Al_2O_3 catalysts, polymerization of $H_2C{=}CH_2$ by supported CrO_x/SiO_2 and methane conversion to aromatic liquids by supported MoO_x/ZSM-5 catalysts.

11:00am **IS+AS+MC+SS-WeM10 Photoelectron Spectroscopy on Ice, Mineral Oxides and Aqueous Solutions of Atmospheric Relevance**, ***Markus Ammann***, Paul Scherrer Institut, Switzerland **INVITED**

Aerosol particles and ice are key in atmospheric chemistry as many chemical and physical processes occurring on and within them are relevant for air pollution and climate. The fundamental understanding of these processes increasingly relies on a molecular level description of structures and mechanisms. This requires tools to access condensed phase – air interfaces with structural and chemical selectivity. Recent advances in pushing the pressure limits of ultrahigh-vacuum surface science methods such as photoelectron spectroscopy have allowed the investigation of environmentally relevant surfaces under nearly ambient conditions and have thereby significantly contributed to the advancement of our understanding of interfaces in the atmosphere. In this overview, recent results on the interaction of acidic gases with ice surfaces, of chemical and photochemical processes on mineral oxides, and of the structure of aqueous solution surfaces will be presented. These examples also demonstrate the instrumental requirements for such in situ experiments, and our recent developments of sample environments to facilitate experiments with environmental substrates will be presented.

11:40am **IS+AS+MC+SS-WeM12 *In Situ* Analysis of Materials Under Mechanical Stress: A Novel Instrument for Simultaneous Nanoindentation and Raman Spectroscopy**, ***Chris Michaels***, *Y.B. Gerbig, R.F. Cook*, NIST

Instrumented indentation or “nanoindentation” is a method that is widely used in the study of the mechanical deformation of materials on small length scales (~ micrometer). Raman spectroscopy is a technique that provides insight into the molecular or crystallographic level processes involved in the mechanical deformation of materials, such as strain build-up, phase transformations and variations in crystallinity. Typically these approaches have been used separately wherein the spectroscopic analysis of the material might take place prior to and after the end of a mechanical transformation. Of course, there is significant interest in *in situ* analyses of materials during mechanical transformation as such an approach promises a richer understanding of the underlying physics than is likely possible with analysis limited to pre- and post-transformation. For example, the ability to follow the path of phase transformations rather than just the endpoints is certainly desirable. Consequently, significant effort has been directed toward the coupling of indentation instruments with various in situ analysis capabilities.

This talk describes the design and operation of a nanoindentation instrument that is coupled with a laser scanning Raman microscope to conduct *in situ* spectroscopic analyses of mechanically deformed regions of optically transparent materials under contact loading. The force transducer of the device allows adjustment of crucial experimental parameters, such as indentation loads and loading rates. An incorporated displacement sensor allows for collection of force-displacement curves comparable to conventional nanoindentation instruments. The device is mounted on the sample stage of an inverted optical microscope that is configured for Raman microscopy, allowing optical access to the mechanically deformed regions of transparent samples. The capabilities of this novel instrument will be demonstrated by *in situ* studies of the indentation-induced phase transformations in an epitaxial silicon-on-sapphire (SoS) thin film, in both a microspectroscopy and a laser scanning Raman imaging configuration.

Surface Science
Room: 309 - Session SS+AS+EN-WeM

Dynamic Processes of Single Atoms and Molecules at Surfaces
Moderator: Arthur Utz, Tufts University, Andrew Gellman, Carnegie Mellon University

8:00am **SS+AS+EN-WeM1 Construction and Manipulation of Individual Functional Molecules: from Reversible Conductance Transition to Reversible Spin Control**, ***Hong-Jun Gao***, Chinese Academy of Science, China **INVITED**

Control over charge and spin states at the single molecule level is crucial not only for a fundamental understanding of charge and spin interactions but also represents a prerequisite for development of molecular electronics and spintronics. While charge manipulation has been demonstrated by gas adsorption and atomic manipulation, the reversible control of a single spin of an atom or a molecule has been challenging. In this talk, I will present a demonstration about a robust and reversible spin control of single magnetic metal-phthalocyanine molecule via attachment and detachment of a hydrogen atom, with manifestation of switching of Kondo resonance. Low-temperature atomically resolved scanning tunneling microscopy was employed. Using density functional theory calculations, the spin control mechanism was revealed, by which the reduction of spin density is driven by charge redistribution within magnetic 3d orbitals rather than a change of the total number of electrons. This process allows spin manipulation at the single molecule level, even within a close-packed molecular array, without concern of molecular spin exchange interaction. This work opens up a new opportunity for quantum information recording and storage at the ultimate molecular limit.

References:

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*In collaboration with Liwei Liu, Kai Yang, Yuhang Jiang, Boqun Song, Wende Xiao, Linfei Li, Haitao Zhou, Yeliang Wang, and Shixuan Du, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

8:40am **SS+AS+EN-WeM3 Single Molecule Origins of Electronic Disorder: Random Conformations of α-NPD Molecules on Au(111)**, ***Daniel Dougherty***, *J. Wang*, *J. Wang*, North Carolina State University

Disorder is an important aspect of modeling organic and polymeric electronic materials. Proper accounting of the effects of disorder both in active layers and at interfaces with contacts determine the detailed current-voltage characteristics in organic thin film devices [1]. Our study seeks to visualize and statistically quantify the disorder in α-NPD films at the single molecule scale. This molecule is a common hole transport material in organic LED's and has been found to exhibit strong disorder in thin film diode geometries [2]. We used scanning tunneling microscopy and spectroscopy to observe numerous surface structures of α-NPD on the (111) surface of Au. These structures are distiguished by different lateral order as well as different local molecular conformations. Random molecular conformations on the surface lead to an statistical distribution of hole transport states that is consistent with the distribution inferred from device analysis. *This work was funded by an NSF CAREER award through DMR-1056861. [1]Tessler et al., Adv. Mater. 21, 2741 (2009) [2] van Mensfoort et al., J. Appl. Phys. 107, 113710 (2010)

9:00am **SS+AS+EN-WeM4 Pt-Cu *Single Atom Alloys* for the Selective Partial Hydrogenation of Butadiene**, ***Felicia Lucci***, *M. Marcinkowski*, *E.C.H. Sykes*, Tufts University

Butene is a common feedstock for polymerization reactions; however, butadiene is a minority impurity that poisons the polymerization catalyst. The selective hydrogenation of butadiene to butene serves to increase the purity of the feedstock without reducing the overall concentration of butene. Therefore, catalysts that selectively hydrogenate butadiene to butene and prevent the hydrogenation of butene to butane are of great interest. Using scanning tunneling microscopy (STM) and temperature programmed desorption/reaction (TPD/R), we show that Pt-Cu single atom alloys catalyze hydrogenation of butadiene to butene with 100% selectivity. The addition of small amounts of Pt (~1%) into Cu reduces the barrier for H_2 dissociation, allowing for the low temperature dissociation of H_2. H atoms spill-over onto the Cu sites increasing the concentration of weakly bound H atoms available for the hydrogenation reaction. The weakly bond H atoms readily hydrogenate butadiene to butene. TPR of co-adsorbed H and butadiene shows the exclusive desorption of reactively formed butene, where the reaction extent is limited by the availability of H on the surface. While the individual, isolated Pt atoms in the Cu terrace activate molecular H_2, they do not induce the decomposition of butadiene as observed on Pt(111) surfaces. The ability to control geometries of atomic ensembles and hence the extent of hydrogenation reactions using *single atom alloys* allows for the production of new and efficient catalysts.

9:20am **SS+AS+EN-WeM5 Toward a Dynamical Understanding of Chemistry at Metal Surfaces**, ***Alec Wodtke***, Max Planck Institute for Biophysical Chemistry **INVITED**

One of our most fundamental scientific challenges is to develop predictive theories of chemistry rigorously grounded in the laws of physics. In 1929, Dirac identified the problem famously in a comment about the importance of quantum mechanics to chemistry… *"The underlying physical laws necessary for the mathematical theory of… …the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble."* Despite electrifying advances in computational power, Dirac is still right. The theory of chemistry requires approximate methods for practical computations.

For the theory of surface chemistry, three central approximations are made, involving the use of: 1) classical mechanics for describing nuclear motion, 2) density functionals for calculating electronic states and the Born-Oppenheimer approximation to separate electronic and nuclear degrees of freedom.

The growing importance of computational surface chemistry motivates us to design rigorous experimental tests of these assumptions. Many fundamental questions arise. Can we trust the Born-Oppenheimer approximation for calculating potential energy surfaces for reactions at metal surfaces? Can we characterize and overcome the weaknesses of density functional theory, for example by developing new wave-function based methods for the solid-state? For all of these reasons, it is important to carefully design experimental tests of the capabilities of modern computational surface chemistry.

Using modern molecular beams methods in state-to-state scattering experiments, we obtain a wealth of observational data characterizing the interactions of molecules with metal surfaces. Emphasizing quantitative comparison to first principles theories, we find that energy conversion can occur by unexpected mechanisms, where the electronically adiabatic approximation separating the time scales of electronic and nuclear motion is found to be invalid. The simplicity of the systems under study provides opportunities for developing new theories that go beyond the Born-Oppenheimer approximation. One important outcome of this is the realization that Born-Oppenheimer breakdown can be induced by simple electron transfer events that are common in surface chemistry.

11:00am **SS+AS+EN-WeM10 Steric Effect in O_2 Chemisorption on Al(111)**, ***Mitsunori Kurahashi***, *Y. Yamauchi*, National Institute for Materials Science (NIMS), Japan

O_2 adsorption on Al(111) has been investigated intensively as the most representative system of surface oxidation. The dynamical process happening on the surface, however, remained unclear. An STM study by Brune et al.[1] has proposed that adsorbed O-atoms are atomic and are well separated each other. Initially, this has been ascribed to the transient mobility driven by the O_2 chemisorption energy ("hot-atom" mechanism)[1], but this mechanism has been found to be unlikely. The abstraction mechanism, in which one O-atom is bound to the surface while the other is ejected, has been proposed alternatively based on the resonance enhanced multi-photon ionization measurement.[2] It is however not evident whether or not the abstraction process is the dominant event at low translational energies (E_0). In addition, the STM study by Schmid et al.[3] has suggested that the adsorbates consist of two O-atoms locating at nearby sites. This cannot be explained by the abstraction mechanism.

In this study, we focused attention to the alignment dependence in the O_2 sticking to clarify the reaction mechanism. A single spin-rotational state-selected [(J,M)=(2,2)] O_2 beam, for which we can specify both the molecular alignment and spin direction relative to the magnetic field, was adsorbed on an Al(111) surface. The results show that O_2 molecules parallel to the surface have much higher sticking probabilities than those perpendicular to the surface at $E_0 < 0.2$ eV. The E_0 dependence of the sticking probability indicates that the dissociation barrier at the perpendicular geometry is about 0.1 eV higher than at the parallel geometry. The present results reveal that the abstraction process, which occurs at the perpendicular geometry, is a minor event at low E_0.[4]

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11:20am **SS+AS+EN-WeM11 Surface Temperature Effects in Methane Dissociation on Ni and Ir Surfaces**, ***Arthur Utz***, *E. Peterson*, *E. Dombrowski*, *E. High*, *E. Nicotera*, Tufts University

Recent transition state and quantum dynamics calculations have suggested an important role for surface atom motion in promoting methane dissociation on transition metals including Ni, Pt, and Ir. Here, we describe state-resolved gas-surface scattering measurement of methane dissociation on Ni(111), Ir(111), and Ir(110)-(1x2). Infrared laser excitation prepares methane in a single excited rotational and vibrational state with a precisely defined internal energy. A supersonic molecular beam provides tight control over the translational energy of the methane molecules. The methane molecules, with their well-defined energy, accentuate the role of surface temperature, and the resulting thermal motion of surface atoms, on reactivity.

The presentation will focus on recent experimental results. On the Ir(110)-(1x2) surface, we observe both precursor-mediated and direct reaction channels for the vibrationally excited (ν_3, v=1) molecules at surface temperatures of 300K or higher. For v=0 molecules, a precursor-mediated pathway appears for surface temperatures above 500K, but not for temperatures of 500K or lower. The abrupt disappearance of the precursor-mediated reaction path correlates with a surface reconstruction to (331) facets that was previously reported to occur at 500K. We will report on measurements that extend the temperature range for the vibrationally excited (ν_3, v=1) molecules to temperatures between 100 and 300K on the Ir(110) surface. We will also report on more recent studies that explore the surface temperature dependence of more highly vibrationally excited methane molecules.

11:40am **SS+AS+EN-WeM12 Activation of C_1-C_9 Alkanes on Pt(111): Importance of Dynamics, van der Waals Interactions, and Gas-Surface Energy Transfer**, ***Jason Navin***, *S.B. Donald*, *G. Cushing*, *I.A. Harrison*, University of Virginia

A variety of dissociative sticking coefficients (DSCs) were measured for alkanes varying in size from methane to nonane on Pt(111) using an effusive molecular beam technique. Thermal equilibrium ($T_g = T_s$) and non-equilibrium ($T_g \neq T_s$) DSC measurements provided information about the gas-surface reactivity and energy transfer. Angle-resolved DSCs, S(700 K; ϑ), measured for methane, ethane, and propane on Pt(111) were used to define thermal DSCs, S(T), and discern dynamical behavior. Methane and ethane DSCs were sharply peaked around the surface normal and were found to have similar dynamical biases away from statistical behavior. Precursor-mediated microcanonical trapping (PMMT) models were used to both analyze and predict DSCs over a wide range of experimental conditions and experiments. It was found that the activation energy for dissociative chemisorption of an alkane scales linearly with its molecular desorption energy from the physisorption well in front of the surface. The molecular desorption energy should be proportional to the van der Waals stabilization energy for the products of dissociative chemisorption. The gas-surface energy transfer increased as the alkane size increased from C_1 to C_9. For alkanes larger than C_4, the gas-surface energy transfer was apparently sufficient to fully thermalize the impinging molecule to the temperature of the surface before reaction such that, $S(T_g{=}300K,T_s) = S(T)$.

12:00pm **SS+AS+EN-WeM13 Shining light on an Important Intermediate Step in Photocatalysis: Probing Polarons in ZnO using Infrared Reflection Absorption Spectroscopy**, ***Fabian Bebensee***, *H. Sezen,* Karlsruhe Institute of Technology, Germany*, A. Nefedov, C. Wöll*, Karlsruhe Institute of Technology

ZnO is a wide-bandgap metal oxide exhibiting various highly desirable physico-chemical properties, among them high photocatalytic activity. As such, it has been widely studied employing virtually all available techniques over the past 50 years.[1] In the context of photoexcitations, primarily excitons have been studied extensively including their very recently reported ultrafast formation dynamics.[2] In photocatalysis, dissociation of excitons into free electrons and holes takes place and therefore the binding energies of the polaronic states become crucial for the subsequent steps on the way to finally transferring an electron or hole onto an adsorbed molecule. Despite their importance in photochemistry (see recent work on TiO_2[3]), very little work has been devoted to these trap states in ZnO. Here, we report a novel approach to study polarons in ZnO single crystal substrates: the polaron traps are populated via UV-light irradiation and then probed using infrared reflection absorption spectroscopy (IRRAS). Upon irradiation, a number of previously unobserved, well-defined and sharp absorption bands appear in the IR-spectra. Among these new features is an absorption-edge like feature that we assign to excitations of electrons from the conduction band into hole polaronic trap states. From their time-dependent intensity, we infer a (temperature-dependent) life time of 25 seconds at 75 K. The implications of these findings for ZnO photochemistry will be discussed.

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Surface Science
Room: 312 - Session SS+AS-WeM

Atomistic Modeling of Surface Phenomena
Moderator: Carol Hirschmugl, University of Wisconsin Milwaukee, Eddy Tysoe, University of Wisconsin-Milwaukee

8:00am **SS+AS-WeM1 Oxidation of Cu Surfaces with Step-Edge Defects: Insights from Reactive Force Field Simulation**, ***Qing Zhu***, *W.A. Saidi, J. Yang*, University of Pittsburgh

Defects on metal surfaces can induce non-canonical oxidation channels that may lead to the formation of novel nanostructures. Cu surfaces have been actively researched in the surface science community due to their wide range of applications in many fields. Recently, *in situ* TEM experiments showed that the oxidation of stepped surfaces promotes the formation of a flat metal-oxide interface through the Cu adatoms detachment from steps and diffusion across the terraces. In order to better understand these results, and to provide a tight bridge between the experiment and theory, we have investigated the Cu (100) oxidation using ReaxFF method as implemented in Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). Using models for both defect-free flat and stepped surfaces, our study shows that the step-edge defects induce markedly different oxidation dynamical behavior compared to the flat surface. Additionally, on the stepped-surfaces, we show that the oxidation of the upper-terrace are more favored than the lower-terrace, which we validated by depositing oxygen homogenously on the surface or by using a biased-mechanism where the oxygen atoms target either the top or lower terraces. This favoring of the oxidation of the top terrace drives Cu diffusion flux from the upper-terrace to the lower-terrace that explains the recent TEM experiments. We additionally show that the oxidation behavior of the stepped Cu (100) bears many similarities with the formation of the metal-oxygen "added-row" structures on the (110) surfaces of several metals. Future studies include the investigation of vicinal surfaces with different morphologies and different metals.

8:20am **SS+AS-WeM2 The Role of Time-scale Analysis in Simulation of ALD and CVD Surface Reaction Kinetics**, ***Raymond Adomaitis***, *E. Remmers, C.D. Travis, D. Arana-Chavez*, University of Maryland, College Park

In this paper, we will describe our research on the mathematical structure of atomic layer deposition (ALD) and chemical vapor deposition (CVD) surface reaction kinetics models. Our primary objective is to investigate the mathematical structure of the differential-algebraic (DAE) systems of equations describing surface reaction species dynamics during these thin-film deposition processes. The research is motivated by the challenges presented by writing a well-posed DAE model for surface reaction species dynamics as well as the difficulties encountered when numerically solving these systems. Using a perturbation analysis approach, we demonstrate that the deposition kinetics decomposes naturally into slow (deposition reactions), fast (equilibrium reactions), and instantaneous (conserved quantities) time scales. A key contribution of our work is the development of a reaction network factorization procedure that partitions the surface reaction and deposition species dynamic balances into the distinct time scale ranges described. Under what conditions this procedure works, understanding the implications of fixed points for dynamic ALD processes, interpreting reaction fluxes, and extending the methods to spatially distributed processes in the context of representative thin-film application domains will be discussed. Physical interpretation of DAE system initial conditions for these surface processes constitutes another important research direction in this project; results will be presented which illuminate alumina ALD growth surface dynamics at the start of each exposure (TMA and water) and purge period.

8:40am **SS+AS-WeM3 Hydrogen Production from Formic Acid on Transition Metals and Alloys: A Selectivity Challenge**, ***Manos Mavrikakis***, *J. Scaranto, J.A. Dumesic, S. Singh, S. Li, J.A. Herron, R. Carrasquillo, L. Roling, B. O'Neill, G. Peng*, University of Wisconsin - Madison **INVITED**

Formic acid (HCOOH) is a simple molecule that is an abundant product of biomass processing and can serve as an internal source of hydrogen for oxygen removal and upgrading of biomass to chemicals and fuels. In addition, HCOOH can be used as a fuel for low temperature direct fuel cells. We present a systematic study of the HCOOH decomposition reaction mechanism starting from first-principles and including reactivity experiments and microkinetic modeling. In particular, periodic self-consistent Density Functional Theory (DFT) calculations are performed to determine the stability of reactive intermediates and activation energy barriers of elementary steps. Pre-exponential factors are determined from vibrational frequency calculations. Mean-field microkinetic models are developed and calculated reaction rates and reaction orders are then compared with experimentally measured ones. These comparisons provide useful insights on the nature of the active site, most-abundant surface intermediates as a function of reaction conditions and feed composition. Trends across metals on the fundamental atomic-scale level up to selectivity trends will be discussed. Finally, we identify from first-principles alloy surfaces, which may possess better catalytic properties for selective dehydrogenation of HCOOH than monometallic surfaces, thereby guiding synthesis towards promising novel catalytic materials.

9:20am **SS+AS-WeM5 Elucidating Atomic-scale Wear Processes in Hydrocarbon-based Materials via Molecular Dynamics and AFM**, ***Judith Harrison***, United States Naval Academy, *T.D.B. Jacobs,* University of Pennsylvania*, P.L. Keating, M. Fallet,* United States Naval Academy*, J.D. Schall,* Oakland University*, Y. Jiang, K.T. Turner, R.W. Carpick,* University of Pennsylvania*, K.E. Ryan*, United States Naval Academy

Molecular dynamics (MD) simulations are unique in their ability to elucidate atomic-scale phenomena because the positions, velocities, and forces of all atoms in the system are known as a function of time. 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. We have performed atomic force microscope (AFM) experiments and MD simulations aimed at examining adhesion and wear in diamond, ultrananocrystalline diamond (UNCD), and amorphous carbon (a-C:H) materials. Specifically, we examined the normal and sliding contact of differently shaped axisymmetric tips, composed of a-C:H and UNCD, with hydrocarbon-based substrates. Specific attention was paid to elucidating specific atomic-scale wear mechanisms and their dependence on tip shape, material, surface termination, impact point, and roughness. To examine the effect of the potential energy function on wear mechanisms, identical simulations were performed with the AIREBO potential and the REBO+S potential. The AIREBO potential is based on the reactive empirical bond-order potential (REBO), which was developed to model CVD growth of diamond. Recently, it was demonstrated that the short-range cut-off for covalent bonding in the REBO potential resulted in bond-breaking forces that are an order of magnitude larger than those predicted by DFT calculations. A screening function was added to the REBO potential (REBO+S) to alleviate this situation. Simulations were carried out using each potential, and wear mechanisms identified in each set of simulations were compared.

9:40am **SS+AS-WeM6 Theoretical Investigation of the Structure and Properties of Titania/Graphene Hybrid Materials**

Ivan Iordanov, *C.J. Karwacki,* Edgewood Chemical And Biological Center*, G.M. Mogilevsky*, Booz Allen Hamilton

We are using modeling to understand the properties of complex materials that show promise for catalysis, filtration and decontamination. These materials are of interests both for chemical defense, as well as in many industrial applications. The main focus of our modeling so far has been determining the structure and properties of mixtures of TiO2 nanoparticles(NPs) and small sheets of graphene. The synthesis technique for these materials was pioneered at ECBC. It involves synthesizing graphene from alizarin molecules in close contact with TiO2 NPs. This was expected to create a close connection between the graphene and TiO2 NPs, and improve their catalytic properties. However, the exact structure of the small graphene patches and how and where they bind to TiO2 is difficult to characterize experimentally. Our models have shown that the binding between graphene TiO2 is quite weak (on the order of 0.01eV/Carbon atom), and that it is not strongly dependant on the addition of O and OH to the surface of the graphene, or to the size of the graphene patches. This appears to confirm the experimental finding that the surface graphene can be removed from the TiO2 particles simply by rubbing. We also modeled the case where graphene is surrounded by TiO2 on both sides, and the binding in this case increases by nearly 2x, suggesting that graphene would prefer to bind between TIO2 NPs. This may be the explanation for the disappearance of the smallest (~5nm) sized pores from the TiO2 NP agglomerates upon addition of graphene. We also find that there is a non-trivial degree of charge transfer between graphene and TiO2, which can be expected to improve TiO2's photo catalytic properties.

11:00am **SS+AS-WeM10 Real-Time Ab-Initio KMC Simulation of the Self-Assembly and Sintering of Bimetallic Epitaxial Nanoclusters: Au+Ag on Ag(100)**

James Evans*, Y. Han, D.-J. Liu*, Iowa State University

Far-from-equilibrium shape and structure evolution of bimetallic epitaxial nanoclusters during formation by deposition or during post-assembly sintering is extremely sensitive to the details of periphery diffusion and intermixing kinetics. Precise characterization requires accurate determination of distinct barriers for many possible local environments (compositions and periphery configurations) of the diffusing adatom. This is achieved for epitaxial nanoclusters using DFT to assess adsorption energies and lateral pair- and trio-interactions both conventionally with adatoms at adsorption at adsorption sites, and unconventionally with an adatom at the transition state for hopping. KMC simulation incorporating these barriers then captures structure evolution on the appropriate time-scale. The approach is applied for unstrained Au-Ag nanoclusters on Ag(100) where these can be assembled with either 2D core-ring by sequential codeposition or intermixed structures by simultaneous codeposition or annealing. This ab-initio level approach replaces typical heuristic analyses, often resorting to macroscopic concepts, e.g., for intermixing kinetics.

11:20am **SS+AS-WeM11 Progress in Characterizing Submonolayer Island Growth: Capture-Zone Distributions, Growth Exponents, and Hot Precursors**

TheodoreL. Einstein*, J.R. Morales-Cifuentes,* University of Maryland, College Park*, A. Pimpinelli*, Rice Quantum Institute

We review previous results for using the capture-zone [island proximity cell] distribution (CZD) in island growth to extract information about the critical nucleus size i.[1] Over the experimentally accessible region, the CZD is well described by the generalized Wigner distribution $P_\beta(s) = a_\beta\, s^\beta \exp(-b_\beta s^2)$, dependent only on the exponent β. For diffusion-limited aggregation (DLA), $\beta \approx i+2$. We discuss recent experimental applications. For comparison with this approach, we consider the corresponding dependence of the growth exponent χ (stable island density $N \sim F^\chi$, where F is the flux) for both DLA and attachment-limited aggregation (ALA). In either case, $\chi\beta = i$, so that for ALA, where $\chi = 2i/(i+3)$, we find $\beta = (i+3)/2$.[2] We compare with experiments depositing pentacene (5A) and p-hexaphenyl (6P) on sputtered mica.

Furthermore, recent experiments[3] studying 5A on amorphous mica gave evidence of nucleation via a hot precursor state, with an unusual relationship between N and substrate temperature. Thus motivated, we examine a model of such behavior.[4] We use rate equations and Walton's relation. We take deposited monomers to be hot initially, traveling ballistically with temperature-independent speed v until a time τ, when they thermalize. For the dimensionless combination $z := v\, \tau\, N^{-1/2} \ll 1$ rapid thermalization occurs, with consequent DLA nucleation. For $z \gg 1$ we find the novel behavior for hot-monomer aggregation (HMA): χ has, unexpectedly, the same form as for ALA. We scrutinize behavior in both limits as well as in the crossover regime $z \sim 1$, in which behavior can be described using an effective χ. At low temperatures, the behavior becomes markedly non-Arrhenius, insensitive to temperature. We conclude a discussion of more general applications of this framework.

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11:40am **SS+AS-WeM12 Molecular Dynamics Simulation of Ge Deposition and Islanding on Amorphous Silica Substrates**

C.Y. Chuang, University of Pennsylvania*, S.M. Han,* University of New Mexico*, **Talid Sinno***, University of Pennsylvania

Selective epitaxial growth (SEG) of Ge on Si substrates has proven to be a versatile pathway for producing Ge substrates to enable III-V device integration on Si. However, persistent problems remain, including dislocation formation and high stresses due to lattice parameter and thermal expansion coefficient mismatches between Si and Ge. Further optimization of the SEG process may be significantly assisted by atomistic simulation. Here, we present an atomistic analysis of Ge deposition on SiO_2. We begin by describing a validation process for a Tersoff-based model for the ternary Si-Ge-O system [1,2], in which we compare simulation predictions to detailed experimental data [3,4] for a variety of properties. Using this validated interatomic potential, Ge deposition and islanding on an amorphous SiO_2 surface is studied with direct molecular dynamics and the results are compared to experimental measurements [4] of island size distributions as a function of deposition rate and temperature. A key aspect of our modeling approach is a procedure to accelerate the simulations. While direct molecular dynamics simulations of Ge deposition on SiO_2 are able to capture Ge island nucleation, growth and coarsening, the very fast deposition rates necessary makes difficult direct comparison to experimental measurements of island density and size distributions. In particular, we show that direct molecular dynamics simulations are able to approach, but not quite reach, the deposition conditions in experiment. The accelerated simulations are based on "equation-free" coarse projective integration [5]. Here, measures of the island size distribution dynamics are obtained from short molecular dynamics simulations and then used to evolve numerically the size distribution over large time intervals. The new island size distribution is then used to reconstruct consistent atomic configurations that are subsequently evolved further with molecular dynamics and the process is repeated. Here, we show that the reconstruction of atomic configurations from size distribution moments represents the key challenge in deposition simulations and we propose approaches for achieving this in a computationally tractable manner.

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12:00pm **SS+AS-WeM13 Dimerization Induced Deprotonation of Water on $RuO_2(110)$**

*R. Mu, D.C. Cantu, V.-A. Glezakou, Z. Wang, I. Lyubinetsky, R. Rousseau, **Zdenek Dohnalek***, Pacific Northwest National Laboratory

RuO_2 has proven to be indispensable as a co-catalyst in numerous systems designed for photocatalytic water splitting. Here we present a first mechanistic study of water adsorption, dissociation, and diffusion on the most stable RuO_2 surface, rutile $RuO_2(110)$. Variable temperature scanning tunneling microscopy (STM) and ab initio molecular dynamics based density functional theory calculations (DFT) are employed to follow the behavior of small water clusters. We show that water monomers adsorb molecularly on Ru sites, become mobile above 240 K, and diffuse along the Ru rows. The monomers readily pair up and form dimers that are immobile below 273 K. Finally, the dimers deprotonate and form Ru-bound H_2O-OH and bridging OH species. This is in a sharp contrast with the molecular binding of water dimers observed on isostructural TiO_2(110). The onset for diffusion of H_2O-OH pairs on 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 diffusion of H_2O-OH pairs is found to proceed *via* a rollover mechanism, with a water molecule moving over OH, followed by hydrogen transfer from H_2O to OH. At high water coverages, water dimers are found to be the building blocks of longer water chains on Ru rows. The observed behavior of water monomers and dimers is compared and contrasted with that previously reported on isostructural rutile TiO_2(110).

In-Situ Spectroscopy and Microscopy Focus Topic
Room: 313 - Session IS+2D+MC+NS+SP+SS-WeA

In-Situ Scanning Microscopy
Moderator: Markus Ammann, Paul Scherrer Institut

2:20pm **IS+2D+MC+NS+SP+SS-WeA1 *In Situ* Studies of Model Fuel Cells**, ***Zhi Liu***, Lawrence Berkeley National Laboratory **INVITED**

The ambient pressure x-ray photoelectron spectroscopy (AP-XPS) endstations based on differentially pumped electron energy analyzers have been recognized by scientific communities as an important in-situ tool to study water, environmental science, catalysis and many other important fields. Multiple new AP-XPS endstations are currently under planning or development at US and international synchrotron light sources. Recently we have installed a new hard x-ray AP-XPS endstation at ALS Beamline 9.3.1 (2.5keV- 5keV). By using X-ray up to 5KeV, we can perform AP-XPS at a pressure up to 110 torr. The probing depth of photoelectrons also increases to >10 nm, which will allow us to study not only the gas/solid interface but also the liquid/solid interface. In this talk, I will give an overview of science projects at ALS BL9.3.2 in heterogeneous catalysis and electro-chemistry using these new systems. Furthermore, I will present results of our in-situ study on the electrolyte/electrode interface of a working model electrochemical cell at ALS BL9.3.1. We believe the successful development of soft and hard X-ray APXPS endstations will provide energy research community a powerful in-situ tool to directly study the electrolyte/electrode interface of many important electrochemical devices.

3:00pm **IS+2D+MC+NS+SP+SS-WeA3 Probing of Nanoscale Objects in Reactive Liquids through Membranes using Near-Field Microwave Microscopy**, ***Alexander Tselev***, Oak Ridge National Laboratory, *A. Komakov*, National Institute of Standards and Technology (NIST)

Many functional objects (and interfaces) have to be studied in situ when the object is immersed in liquid environment. In addition, for energy, chemical, (bio-) medical and other applications, there is a need to study the encapsulated objects, which otherwise can be chemically reactive or toxic. These samples are often mesoscopically small or exist in minuscule quantities. Recently, we have developed a process for preparation of liquid-filled cells sealed with ultrathin membranes. Such cells can be implemented for in-situ studies using, for example, electronor soft x-ray microscopy due to a high transparency of these membranes to electron beams. However, in many cases electron microscopy is an invasive technique due to various electron beam induced parasitic effects (e.g. radiolysis or beam induced deposition). To overcome these impediments, we demonstrate the scanning microwave impedance microscopy (sMIM) to image different nanoscale objects immersed in the liquid environment through 30 nm SiN membranes. In the sMIM, microwaves of a frequency of 3 GHz are sent through a coaxial cable connected to a shielded cantilever probe fully compatible with an AMF microscope. The sharp probe tip provides “focusing effect” for the electric component of the microwave. For imaging, the tip is brought into gentle mechanical contact with a membrane. Amplitude and phase of microwaves reflected from the probe are monitored. Since the wave reflection is dependent on the tip-sample system impedance, reflected waves carry information about sample local properties. The effective distance into the sample depth, where the tip-induced field enhancement takes place, is approximately equal to the tip apex radius. Since the membrane thickness is smaller compared to the tip radius of a typical probe (about 50 nm for a fresh tip), the tip-sample impedance is dependent on the dielectric properties of the material beneath membrane, and therefore, it is possible to “see” through the membrane. We demonstrate imaging of different combinations of model liquids and nanoparticles: water and water-based solutions (ε~80), organic solvents (ε~10-25), and oils (ε~2-3) containing Ni metal, polystyrene (ε~2.5) and PbO (ε~25) particles. This technique can be further implemented for a broad range of objects in confined liquids, and can be used to monitor interfacial electrochemical reactions. Imaging with sMIM was performed at CNMS, which is sponsored at ORNL by the SUFD, BES, US DOE.

4:20pm **IS+2D+MC+NS+SP+SS-WeA7 Caught in the Act! Live Observations of Catalysts Using High-Pressure Scanning Probe Microscopy**, ***Irene Groot***, Huygens-Kamerlingh Onnes Laboratory, Leiden University, Netherlands **INVITED**

Recently it has become clear that essential differences can exist between the behavior of catalysts under industrial conditions (high pressure and temperature) and the (ultra) high vacuum conditions of traditional laboratory experiments. Differences in structure, composition, reaction mechanism, activity, and selectivity have been observed. These observations indicated the presence of the so-called pressure gap, and made it clear that meaningful results can only be obtained at high pressures and temperatures. However, most of the techniques traditionally used to study catalysts and their reactions were designed to operate under (ultra) high vacuum conditions. To bridge the pressure gap, the last years have seen a tremendous effort in designing new instruments and adapting existing ones to be able to investigate catalysts *in situ* under industrially relevant conditions.

This talk focuses on the development of scanning probe microscopy for *operando* observations of active model catalysts. In our group, we have developed set-ups that combine an ultrahigh vacuum environment for model catalyst preparation and characterization with a high-pressure flow reactor cell, integrated with either a scanning tunneling microscope or an atomic force microscope. With these set-ups we are able to perform atomic-scale investigations of well-defined model catalysts under industrial conditions. Additionally, we combine the structural information from scanning probe microscopy with time-resolved mass spectrometry measurements on the gas mixture that leaves the reactor. In this way, we can correlate structural changes of the catalyst due to the gas composition with its catalytic performance.

This talk highlights a short overview of the instruments we developed and illustrates their performance with results obtained for different model catalysts and reactions. As a proof of principle, results for the fruit fly of surface science, *i.e.* CO oxidation, will be shown. But additionally, results for more complex reactions such as NO reduction, Fischer-Tropsch synthesis, desulphurization, and production of chlorine will be discussed.

5:00pm **IS+2D+MC+NS+SP+SS-WeA9 X-ray Photoelectron Spectroscopy Studies of H_2O Dissociation on Pre-oxidized Al (111) and Cu (111) Single Crystal Surface**, ***Qianqian Liu***, SUNY, Binghamton University, *X. Tong*, Brookhaven National Laboratory, *G.W. Zhou*, SUNY, Binghamton University

Dissociation of H_2O molecules on ultrathin oxide overlayers formed on metal surfaces plays a critical role in many catalytic reactions. However, the effects of chemical states and thickness of oxide overlayers on the microscopic process of H_2O dissociation are still poorly understood. In this work, X-ray photoelectron spectroscopy (XPS) is employed to study H_2O dissociation on oxidized Al (111) and Cu (111) surfaces with controlled chemical states and thicknesses of the oxide films. For Al (111), the experiment was performed under two water vapor pressures (10^{-6} Torr and 5 Torr) on aluminum oxide films with the thicknesses varying from 2.47 Å to 5.14 Å; for Cu (111), the experiment was performed by varying the water vapor pressure from 10^{-7} Torr to 10^{-5} Torr and temperature from 100°C to 450°C on the oxide film with a constant thickness. Al (2p), Cu (2p), Cu (LMM) and O (1s) spectra were monitored by XPS after each oxygen exposure followed by subsequent H_2O exposure. Upon exposing the oxide to water vapor, the O (1s) peak shifts to a higher energy and becomes broader. A detailed analysis of the spectra indicates that H_2O molecules dissociate into OH groups for both oxidized Al and Cu surfaces. However, the subsequent reaction of OH groups with the oxide films on Cu (111) and Al (111) surfaces are dramatically different. On the oxidized Al(111) surface, OH is further incorporated into the aluminum oxide that results in the thickening of the oxide film, whereas on the oxidized Cu (111) surface, OH works as a reducing agent to remove oxygen from the oxide film that results in the thinning of the Cu oxide film. The microscopic processes underlying the differences in H_2O dissociation on oxidized Al (111) and Cu (111) will be described in detail.

5:20pm **IS+2D+MC+NS+SP+SS-WeA10 Operando APXPS of the Liquid-Solid Interface: Au Oxidation**, ***Ethan Crumlin***, *S.A. Axnanda, P.N.R. Ross, Z.L. Liu*, Lawrence Berkeley National Laboratory

Interfaces play an important role for many reaction processes and are essential for electrochemistry. Electrochemical systems ranging from high temperature solid oxide fuel cells (SOFC) to lithium ion batteries to capacitors have a wide range of important interfaces between solids, liquids, and gases which play a pivotal role in how energy is stored, transferred, and/or converted. Previous capabilities of ambient pressure X-ray Photoelectron Spectroscopy (APXPS) have primarily only been able to observe the gas-solid and gas-liquid interfaces. However, recent enhancements now enable new APXPS systems to work at pressures larger then 20 Torr, and utilize ‘Tender’ X-rays (2.5 – 7 keV). These features provide new capabilities and opportunities for probing the liquid-solid and solid-solid interfaces. Using synchrotron X-rays at Lawrence Berkeley National Laboratory, the Advanced Light Source and our ‘Tender’ X-ray APXPS endstation that is outfitted with various *in situ/operando* features such as electrical leads to apply electrical potentials and operates at pressures >20 Torr, to observe the liquid-solid interface of a gold foil electrode that has been immersed and partially removed from a liquid electrolyte. This talk will provide details on how we used this technique to probe liquid-solid interface and in real-time observe the oxidation of the gold foil electrode under varying applied potentials and different electrolyte solutions.

5:40pm **IS+2D+MC+NS+SP+SS-WeA11 Water on ZnO(10-10) Investigated by Ambient Pressure X-ray Photoelectron Spectroscopy**, ***Chris Goodwin***, University of Delaware, *A. Boscoboinik*, Brookhaven National Lab, *C. Arble, J.T. Newberg*, University of Delaware

The extent to which ZnO hydroxylates under ambient conditions can significantly influence catalytic properties. Thus, it is critical to understand the composition of different ZnO terminations as a function of relative humidity (RH) in order to elucidate the true interfacial surface terminations. In this talk we present results of ambient pressure XPS (APXPS) for water exposures to a ZnO(10-10) single crystal. It will be shown that ZnO(10-10) extensively hydroxylates at the interface, and both molecular and dissociative water increase as the RH increases. These results are consistent with simulations in the literature that highlight the efficacy for ZnO(10-10) to dissociate water.

Scanning Probe Microscopy Focus Topic
Room: 312 - Session SP+AS+BI+NS+SS-WeA

Advances in Scanning Probe Microscopy

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

2:20pm **SP+AS+BI+NS+SS-WeA1 Majorana Mode in Vortex core of $Bi_2Te_3/NbSe_2$Topological Insulator-Superconductor Heterostructure**, ***Jinfeng Jia***, Shanghai Jiao Tong University, China **INVITED**

Majorana fermions have been intensively studied in recent years for their importance to both fundamental science and potential applications in topological quantum computing[1,2]. Majorana fermions are predicted to exist in a vortex core of superconducting topological insulators[3]. However, they are extremely difficult to be distinguished experimentally from other quasiparticle states for the tiny energy difference between Majorana fermions and these states, which is beyond the energy resolution of most available techniques. Here, we overcome the problem by systematically investigating the spatial profile of the Majorana mode and the bound quasiparticle states within a vortex in $Bi_2Te_3/NbSe_2$[4] by using *in situ* ultra-low temperature STM/STS. While the zero bias peak in local conductance splits right off the vortex center in conventional superconductors, it splits off at a finite distance ~20nm away from the vortex center in $Bi_2Te_3/NbSe_2$, primarily due to the Majorana fermion zero mode. While the Majorana mode is destroyed by reducing the distance between vortices, the zero bias peak splits as a conventional superconductor again. This work provides strong evidences of Majorana fermions and also suggests a possible route to manipulating them.

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* In cooperation with Jin-Peng Xu, Mei-Xiao Wang, Zhi Long Liu, Jian-Feng Ge, Xiaojun Yang, Canhua Liu, Zhu An Xu, Dandan Guan, Chun Lei Gao, Dong Qian, Ying Liu, Qiang-Hua Wang, Fu-Chun Zhang, Qi-Kun Xue

3:00pm **SP+AS+BI+NS+SS-WeA3 Robust Protection from Backscattering in the Topological Insulator $Bi_{1.5}Sb_{0.5}Te_{1.7}Se_{1.3}$**, ***Fumio Komori***, *S. Kim, S. Yoshizawa, Y. Ishida,* University of Tokyo, Japan, *K. Eto, K. Segawa,* Osaka University, Japan, *S. Shin,* University of Tokyo, Japan, *Y. Ando*, Osaka University, Japan

Three-dimensional (3D) topological insulators (TIs) are accompanied by gapless surface states due to a nontrivial Z_2 topology of the bulk wave functions. The topological surface state (TSS) of a 3D TI is helically spin polarized, which leads to a suppression of electron scatterings due to spin mismatch between the eigenstates before and after the scattering. The suppression has been inferred from the measurements of quasiparticle interference (QPI) using scanning tunneling microscopy. No QPI was observed for intraband scatterings within unwarped TSSs. However, it has not been clear to what extent the scattering is suppressed within TSS.

In the present study, we have elucidated how the elastic scattering is suppressed as a function of the scattering angle and electron energy in the helically-spin-polarized surface electrons in a single and unwarped upper Dirac cone of $Bi_{1.5}Sb_{0.5}Te_{1.7}Se_{1.3}$. In this material [1], E_F is located very close to the Dirac energy E_D. We compared the scattering wave vectors observed at 5 K with the diameters of the constant-energy contours of the unoccupied TSS which was measured by using time-resolved ARPES implementing a pump-probe method. Moreover, the inelastic scattering time of unoccupied TSS was directly obtained by this method.

At the energy above E_D, we found that there is a sharp threshold for the length of the scattering vector, above which the observed QPI intensity is abruptly diminished [2]. Such a threshold indicates the existence of a well-defined critical scattering angle beyond which elastic scattering is suddenly suppressed. The observed protection from backscattering in the TSS occurs not only for 180° but also for a wide range of angles between 100° and 180°. Such a wide angle range for the protection from backscattering is found to be essentially independent of the energy up to 300 meV above E_D until the Dirac cone becomes warped and/or the bulk scattering events intervene. At energies higher than 300 meV, we found hexagonal patterns in the FT-QPI images that come from warping of the TSS Dirac cone. In this energy range, the critical scattering vector was not clearly observed, indicating a different mechanism of the protection from backscattering in the warped Dirac cone. The observed inelastic scattering lifetime of TSS is longer than 10 psec just above E_F. The robust protection from the backscattering and long inelastic scattering in the TSS strongly support the possible applications for electronics and spintronics using weak electron scattering of TSS at E_F.

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3:20pm **SP+AS+BI+NS+SS-WeA4 Measurements and Analysis of Sub Nanometer Stepped Surfaces Using a Traceable Atomic Force Microscope**, ***Ndubuisi Orji***, National Institute of Standards and Technology (NIST), *S. Gonda,* AIST, Japan, *R.G. Dixson*, National Institute of Standards and Technology (NIST)

Although scanning probe microscopes are used in a wide variety of nanoscale measurements, the issue of instrument characterization, accuracy and calibration, continue to be a limiting factor in interpreting the resulting data. In order to accurately characterize dimensional linearity and accuracy at the sub-nanometer range, samples and robust analysis techniques suited to measurements at this range should be used.

Using Al_20_3 surfaces on the c(0001), a(110), and r(102) planes, and robust analyses techniques, we evaluate stepped surfaces for linearity characterization at the nanoscale. Measurements were performed using a traceable atomic force microscope (T-AFM) with displacement interferometry in all three axes. The T-AFM, which has a metrology scanning stage monitored in six axes, is housed in a mini environment with a long term temperature range of less than 2 mK, and serves as a stable platform to develop calibration standards.

The smallest of the features Al_20_3 c(0001) with a height of 0.22 nm shows a combined uncertainty of 0.01 nm, with a linearity of 0.009%. The intrinsic traceability of the T-AFM (through displacement interferometer to the *SI* meter) provides additional verification to the size naturally occurring steps of the Al_20_3 and other samples used. The results show that robust and stable linearization and calibration procedures could be developed for sub nanometer SPM characterization with low uncertainty. This will enable and support accurate dimensional characterization of scientifically relevant surfaces.

4:20pm **SP+AS+BI+NS+SS-WeA7 Direct Observation of Edge States of 1D and 2D Topological insulators**, ***Han Woong Yeom***, Institute for Basic Science, Republic of Korea **INVITED**

1D and 2D toplogical insulators (TI's) are characterized by 0D and 1D edge states of exotic spin-charge characteristics. In this talk, we introduce the first direct real space observations of such 0D and 1D edge channels of 1D and 2D TI's by scanning tunneling microscopy/spectroscopy. The 1D TI utilized is the charge density wave phase of In atomic wires formed on the Si(111) surface, which we discovered in 1999. We clearly identified, topographically and spectroscopically, two different soliton excitations along the wires. The unique features of these solitons, theoretically unraveled as chiral solitons of the Z_4 topology, are discussed. On the other hand, a Bi(111) bilayer was theoretically predicted as a 2D TI in 2005. We have grown Bi(111) bilayer nanoislands with zigzag edges on the surface of Bi_2Te_2Se. Along those edges, we identified the edge localized electronic state in accordance with first principle calculations. The unexpected electronic structures of the epitaxial Bi(111) bilayer and the Bi/Bi_2Te_2Se interface are discussed. These two findings pave the avenue towards the microscopic study and the nanoscale utilization of topological solitons and quantum spin Hall states.

5:00pm **SP+AS+BI+NS+SS-WeA9 Controlling Charges of the Dipole Layer at Metal-Semiconductor Interfaces**, ***Tae-Hwan Kim***, Pohang University of Science and Technology, Republic of Korea, *H.W. Yeom*, Pohang University of Science and Technology and Institute for Basic Science, Republic of Korea

Metal-semiconductor interfaces have drawn a lot of interest in the field of semiconductor surface and interface science, and have been one of the most essential parts in semiconductor electronic and optoelectronic devices. For example, the Schottky-barrier height experimentally observed at the metal-semiconductor interface appears to be nearly independent of the work function of the metal. Since the time of Bardeen, interface gap states seem to have been a primary mechanism of the Schottky-barrier height causing Fermi level pinning at metal-semiconductor interfaces. Recently, polarized chemical bonds at metal-semiconductor interfaces have been recognised to lead to the apparent Fermi level pinning effect. When these interface bonds are formed underneath thin metal islands grown on a silicon substrate, a spontaneous charge transfer across the semiconductor-metal interfaces occurs as a result of the difference in the Fermi level positions between the metal and the semiconductor. These polarized chemical bonds can form a dipole layer. This dipole layer can play an important role in many areas of technology, for instance, in organic light emitting diodes. However, some of the fundamental aspects of the charge injection process into/from the interface dipole layer at the Schottky contact are yet not explored in any real detail.

In this work, we report the use of scanning tunneling microscopy (STM) to form a double-barrier tunneling junction (DBTJ) with thin metallic nanoislands grown on Si(111) and to control charges of the interface dipole layer formed between the metallic nanoislands and the Si(111) substrate. Reversible hysteric switchings in their $I-V$ and differential conductance spectra are observed due to the charging and discharging of the interface dipole layer in a similar fashion to molecular DBTJs. STM images clearly visualize the distinct charge states and scanning tunneling spectroscopy (STS) spectra reveal that quantum well states (QWSs) of the ultrathin islands act as the charging/discharging channels in analogy to the molecular orbitals in the case of the molecular DBTJs. This work demonstrates that the charges of the interface dipole layer at the nanoscale Schottky contact can be controlled by the electron transfer via the QWSs of the metallic islands.

5:20pm **SP+AS+BI+NS+SS-WeA10 Advances in Imaging and Quantification of Electrical Properties at the Nanoscale using Scanning Microwave Impedance Microscopy (sMIM)**, ***Stuart Friedman***, *Y. Yang, O. Amster,* PrimeNano, Inc, *S. Johnston*, Stanford University

Scanning Microwave Impedance Microscopy (sMIM) is a novel mode for AFM-enabling imaging of unique contrast mechanisms and measurement of local permittivity and conductivity at the 10's of nm length scale. Custom shielded AFM probes enable the system to use microwaves to probe the impedance of the tip sample interface and extract information on local electrical properties of the sample. After introducing the theory of operation, we will review the state of the art, including imaging studies of microelectronic devices as well as novel materials and nanostructures, such as graphene and patterned optical crystals and ferro-electrics. These studies reveal novel information about doping distributions, domains, domain walls and other features. In addition to imaging, the technique is suited to a variety of metrology applications where specific physical properties are determined quantitatively. We will present research results on quantitative measurements of dielectric constant (permittivity) and conductivity (e.g. dopant concentration) for a range of materials. For samples where properties such as dielectric constant are known the technique can be used to measure film thickness.

5:40pm **SP+AS+BI+NS+SS-WeA11 Scanning Photocurrent Microscopy on MoS_2, $MoS_{2(1-x)}Se_{2x}$, and $MoSe_2$ Monolayer Islands and Films Grown by CVD**, ***Velveth Klee***, *D. Barroso, E. Preciado,* University of California - Riverside, *K. Erickson,* Sandia National Laboratories, *M. Triplett,* University of California -Davis, *C. Lee, A. Nguyen, I. Lu, S. Bobek, J. Mann,* University of California - Riverside, *A. Talin, F. Leonard,* Sandia National Laboratories, *L. Bartels*, University of California - Riverside

We presents scanning photocurrent measurements on CVD-grown monolayer films of molybdenum disulfide, molybdenum diselenide and the alloys of these materials. Our experiments reveal a pronounced effect of the current on excitation in the gap region between contacts, as opposed to directly at the electrodes. Measurements at different irradiation intensity, irradiation position and bias shed light on the charge transfer processes in this material system. Thermal effects are ruled out by complementary measurements of thermal transport using infrared imaging.

Surface Science
Room: 309 - Session SS-WeA

Chirality and Enantioselectivity on Surfaces
Moderator: Melissa A. Hines, Cornell University, Andrew Teplyakov, University of Delaware

2:20pm **SS-WeA1 Simple Rules and the Emergence of Chirality at Surfaces**, ***Rasmita Raval***, University of Liverpool **INVITED**

Chiral surfaces can be created by the adsorption of intrinsically chiral molecules, with the handedness defined by the molecule [1-4]. Additionally, a second manifestation of chirality may arise due to the molecule-substrate interaction in the form of chiral adsorption footprints. Recent advances have allowed both levels of chirality to be determined at the single-molecule level [5-8] and, surprisingly, reveal a wide range of chiral orderings. How both these aspects unfold and express themselves in organized molecular layers at surfaces is little understood. This talk will illustrate how the emergence of chirality in organised assemblies of amino-acids on a Cu(110) surface can be understood in terms of simple generic rules.

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3:00pm **SS-WeA3 Exploring Enantioselectivity on Chirally Modified Surfaces in Ultrahigh Vacuum**, ***Wilfred T. 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 amino acids on Pd(111). Scanning tunneling microscopy (STM) reveals that some amino acids form tetrameric units, and others form dimers. Only those amino acids 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.

3:20pm **SS-WeA4 The Structure Sensitivity of L and D Tartaric Acid Explosive Decomposition on Copper Surface Structure Spread Single Crystals**

***Aaron Reinicker**, B.S. Mhatre, B.S. Holsclaw,* Carnegie Mellon University*, E.C.H. Sykes,* Tufts University*, A.J. Gellman*, Carnegie Mellon University

There are many catalytic reactions that are sensitive to the surface structure of the catalyst. Surface Structure Spread Single Crystals (S^4Cs) expose a continuous distribution of crystal planes across their surfaces. Each point on the S^4Cs has a different local crystallographic orientation that can be determined from the shape of the S^4Cs and the orientation of its bulk crystal lattice vectors. Crystal planes on these S^4Cs contains terraces, monatomic steps, and kinks and can be described as chiral with an R or an S orientation. When coupled with spatially resolved surface analysis techniques, S^4Cs can be used to study the effects of surface structure and chirality on surface chemistry across a broad, continuous distribution of crystal planes. In this work, the structure sensitivity of L and D tartaric acid explosive decomposition was studied using a Cu(111)±10° S^4C. Isothermal Temperature Programmed Desorption (TPD) was used in which each sample was held at a temperature >20 K below the temperature of peak decomposition observed in a standard (TPD) experiment until the decomposition reaction occurred. Spatially resolved X-ray Photoelectron Spectroscopy (XPS) was performed to determine which crystal planes on the Cu(111)±10° S^4C had undergone explosive decomposition after quenching the temperature of the sample at the decomposition peak during an isothermal TPD. Quenching the sample at different times during the isothermal TPD decomposition peak was implemented to visualize the stages of reaction on the Cu(111)±10° S^4C surface. It was found that both D-tartaric acid and L-tartaric acid reacted on crystal planes with (100) steps before crystal planes with (111) steps and the surface structure had more of an effect on the explosive decomposition of tartaric acid than the surface chirality.

4:20pm **SS-WeA7 Ordering of L-alaninate Superstructures on Cu(001)**

***Erkan Ciftlikli**, B.J. Hinch*, Rutgers University

Multiple domains of a c(4x2) superstructure are produced following dissociative L-Alanine adsorption on Cu(001) at temperatures of 0 °C and above. The anticipated structure at 0.25ML relies on stabilization of a tridendate surface species, in ordered arrays, held together with intermolecular H bonding. He atom diffraction is benign, and the films can be investigated over the course of days. The saturated c(4x2) structure is stable up to ~200°C. In contrast the subsaturation surfaces are thermally unstable and a slow relaxation occurs after nucleation of c(4x2) domains. He-surface bound state resonances are seen to affect the symmetries of the He diffraction intensities and the inelastic He-phonon cross sections observed from the chiral adsorbate. The enhanced inelastic scattering intensities are used to compare the vibrational characteristics of saturated and sub-saturation L-Ala/Cu(001) surfaces.

4:40pm **SS-WeA8 Quantitation of Enantiospecific Adsorption on Chiral Nanoparticles from Optical Rotation**

***Nisha Shukla**, N. Ondeck, N. Khosla, A.J. Gellman*, Carnegie Mellon University

Au nanoparticles modified with enantiomerically pure D- or L-cysteine have been shown to serve as enantioselective adsorbents of R- and S-propylene oxide [1]. A simple adsorption model and accompanying experimental protocol have been developed to enable optical rotation measurements to be analyzed for quantitative determination of the ratios of the enantiospecific adsorption equilibrium constants of chiral species on the surfaces of chiral nanoparticles, $(K^{S}_{L}/(K^{S}_{D})=(K^{R}_{D})/(K^{R}_{L})$. This analysis is robust in the sense that it obviates the need to measure the absolute surface area of the absorbent nanoparticles, a quantity that is somewhat difficult to obtain accurately. This analysis has been applied to optical rotation data obtained from solutions of R- and S-propylene oxide, in varying concentration ratios, with D- and L-cysteine coated Au nanoparticles, in varying concentration ratios [2].

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5:00pm **SS-WeA9 Low-Temperature STM Observation of Asymmetrical Adsorption and Chirality of Ga Adatoms on Wurtzite GaN(000-1)**

***Khan Alam**, A. Foley, J. Corbett, Y. Ma, J. Pak, A.R. Smith*, Ohio University

A sample with atomically flat terraces having the c(6×12) reconstruction on GaN(000-1) surface is grown by molecular beam epitaxy and studied at liquid helium temperature using scanning tunneling microscopy. Being the most Ga-rich reconstruction (corresponding to the Ga stability limit) occurring on the N-polar GaN surface,[1] low-temperature STM imaging reveals new details of the c(6×12), although not inconsistent with the early model.[2] Unexpectedly however, a dilute concentration (0.0031 ML) of single atomic adsorbates not seen at room temperature is found covering the terraces. The coverage is stable with time and increases with Ga flux during growth. These adsorbate features are thus attributed to the condensation of Ga adatoms which at room temperature would be in a 2D gas-like state at the surface. Surprisingly, the Ga adsorbates manifest at ~+2.5 V sample bias as distinct L-shapes which are always in one of two possible orientations with respect to <10-10>. Furthermore, on any given atomic terrace, the probability of finding one of the two L-shape orientations is 80%, reversing across a step. However, no in-plane rotation will result in the opposite handed-ness of an L-shape, on either terrace. The L-shaped adsorbates thus reveal broken chiral symmetry linked to adsorption probability, which is attributed to symmetry breaking of the c(6×12) reconstruction.

5:20pm **SS-WeA10 Enantioselectivity and Auto-Amplification by Adsorption**

***Andrew Gellman**, Y. Yun*, Carnegie Mellon University

Metal surfaces can be rendered chiral by cleavage along low symmetry planes of the bulk metal lattice. Their chirality results in the enantioselective adsorption of chiral molecules from racemic mixtures. This work has developed and applied a ^{13}C isotopic labeling method for mass spectrometric detection and quantification of enantiospecific adsorption on chiral surfaces. Enantiomerically pure chiral compounds in which one enantiomer is available in an isotopically labelled form allow the design of experiments in which one can expose chiral or achiral surfaces to mixtures of varying enantiomeric excess in the gas phase (ee_g) and then use mass spectrometry to determine enantiomeric excess on the surface (ee_s).

Exposure of a racemic mixture of D-aspartic acid and ^{13}C-L-aspartic acid to the chiral $Cu(3,1,17)^{R\&S}$ surfaces results in the adsorption of a non-racemic monolayer because of the selective adsorption of one enantiomer over the other. ^{13}C-labeling allows mass spectrometry to distinguish the two enantiomers during desorption from the surface.

These measurements have been used to quantify the enantiospecific adsorption equilibrium constants and the enantiospecific difference in the free energies of adsorption of D- and L-aspartic acid on the chiral $Cu(3,1,17)^{R\&S}$ surfaces.

Not surprisingly, exposure of a racemic mixture of D- and ^{13}C-L-aspartic acid to the achiral Cu(111) results in the adsorption of a racemic mixture; in other words, a gas phase mixture with $ee_g = 0$ results in an adsorbed mixture with $ee_g = 0$. However, exposure of the achiral Cu(111) surface to a gas phase mixture with $ee_g = 0.2$ results in an adsorbed phase with $ee_s = 0.4$. In spite of the fact that the surface is achiral adsorption results in auto-amplification of enantiomeric excess. Although the mechanism of auto-amplification has not been confirmed, one can show that this can be a simple consequence of adsorption of gas phase monomers in the form of homochiral clusters L_n or D_n.

In general, during adsorption on chiral surfaces, the phenomena of enantiospecific adsorption and auto-amplification must be occurring and either competing or augmenting one another.

2D Materials Focus Topic
Room: 310 - Session 2D+AS+HI+NS+SS-ThM

Nanostructures including 2D Heterostructures, Patterning of 2D Materials
Moderator: Kirill Bolotin, Vanderbilt University

8:00am **2D+AS+HI+NS+SS-ThM1 Stitching and Stacking for Atomically Thin Circuitry***, **Jiwoong Park***, Cornell University **INVITED**

The development of large scale growth methods based on chemical vapor deposition (CVD) has enabled production of single-atom-thick films with diverse electrical properties, including graphene (conductor), h-BN (insulator), and MoS2 (semiconductor). Precise vertical stacking and lateral stitching of these 2D materials will provide rational means for building ultrathin heterostructures with complex functionality. However, large scale production and control of these structures requires new characterization and fabrication approaches. In this talk, I will first discuss the structure and physical properties unique to CVD graphene in single and bilayers. Using the atomic-resolution imaging as well as a dark-field transmission electron microscopy (TEM) technique, our group investigated the structure of grain boundaries in CVD graphene and its impact on the mechanical, electrical, and chemical properties. This allowed us to produce CVD graphene with optimized electrical properties. We also reported a new patterned regrowth method to fabricate 2D lateral heterojunctions entirely made of graphene and h-BN, which enables the development of atomically thin integrated circuitry. If time allows, I will also discuss our recent results on the large scale growth of high quality single layer MoS2 as well as graphene film with a uniform lattice orientation. Our characterization and growth approach would ultimately allow the fabrication of electrically isolated active and passive elements embedded in continuous, one-atom-thick sheets, which could be manipulated and stacked to form complex devices at the ultimate thickness limit.

8:40am **2D+AS+HI+NS+SS-ThM3 Vertical and Lateral Heterostructures of Carbon Nanomembranes (CNMs) and Graphene**, ***Andreas Winter***, University of Bielefeld, Germany, *M. Woszczyna, R. Stosch, T. Weimann, F. Ahrelrs,* Physikalisch-Technische Bundesanstalt, Germany, *A. Turchanin*, University of Bielefeld, Germany

Heterostructures of graphene with other 2D materials are of great interest for nanoscience and nanotechnology. However, their fabrication is still not a trivial task. Here we present the engineering and characterization of (i) vertical and (ii) lateral heterostructures of molecular thin (~1 nm) dielectric carbon nanomembranes (CNMs) made of aromatic molecules [1] and single-layer (SLG) graphene sheets. (i) The vertical CNM/SLG heterostructures with terminal amino-groups (NH_2-) are assembled via the mechanical transfer onto oxidized silicon wafers. We show by complementary spectroscopy and microscopy techniques as well as by electric transport measurements that functional amino groups are brought into close vicinity of the SLG sheets and that electric transport of the SLG is not impaired by this assembly, leading to the non-destructive chemical functionalization of graphene [2]. (ii) *The lateral heterostructures* are engineered using electron-irradiation-induced crosslinking of SLG sheets with CNMs. We demonstrate reliable production of well-defined laterally patterned CNM-SLG heterostructures of various sized and architectures on solid substrates and as free-standing sheets, and characterize their properties by Raman spectroscopy and helium ion microscopy.

[1] A. Turchanin and A. Gölzhäuser, Carbon nanomembranes from self-assembled monolayers: Functional surfaces without bulk. *Prog. Surf. Sci.* 87, 108-162 (2012)

[2] M. Woszczyna et al., All-carbon vertical van der Waals heterostructures: Non-destructive functionalization of graphene for electronic applications. *Adv. Mater.* 26 (2014) DOI: 10.1002/adma.201400948

9:00am **2D+AS+HI+NS+SS-ThM4 Gate Tunable Carbon Nanotube - Single Layer MoS$_2$ p-n Heterojunctions**, ***Deep Jariwala****, *V.K. Sangwan, C.-C. Wu, P.L. Prabhumirashi, M.L. Geier, T.J. Marks, L.J. Lauhon, M.C. Hersam*, Northwestern University

The isolation of graphene and the subsequent reports on its electronic properties have spurred tremendous interest in a variety of two dimensional (2D) materials for electronic device applications. Layered semiconducting transition metal dichalcogenides (TMDCs) of Mo and W have emerged as promising alternatives to graphene for optoelectronic applications due to their finite band gap in the visible portion of the electromagnetic spectrum.[1] The atomically thin structure of these 2D materials coupled with van der Waals bonding between adjacent layers allows their stacking into atomically sharp heterostructures with defect-free interfaces, in contrast to epitaxially grown III-V semiconductor heterostructures where the material choices are constrained by lattice matching. Additionally, the few atom thickness of the individual layers enables doping modulation of the overlying layers in a heterostructure using a global back gate. While a large number of heterostructure devices employing graphene have been reported, it's gapless band structure prevents the formation of a large potential barrier for charge separation and current rectification. Consequently, a p-n heterojunction diode derived from ultrathin materials is notably absent and significantly constrains the fabrication of complex electronic and optoelectronic circuits. Here we demonstrate a gate-tunable p-n heterojunction diode using semiconducting single-walled carbon nanotubes (s-SWCNTs) and single-layer molybdenum disulphide (SL-MoS$_2$) as atomically thin p-type and n-type semiconductors, respectively. The vertical stacking of these two direct band gap semiconductors forms a heterojunction with electrical characteristics that can be tuned with an applied gate bias over a wide range of charge transport behavior, ranging from insulating to rectifying with forward-to-reverse bias current ratios exceeding 10^4. In addition, the gate-dependent characteristics of this diode exhibit a unique *'anti-ambipolar'* behavior with two off-states at either extremes of the gate voltage range and a maximum on-state current between them. This heterojunction diode also responds to optical irradiation with photoresponse time < 15 μs.[2] We anticipate that the novel properties and characteristics of this p-n heterojunction can be widely generalized to other atomically thin materials systems.

REFERENCES:

1. Jariwala, D. et al. Emerging Device Applications for Semiconducting Two-Dimensional Transition Metal Dichalcogenides. ***ACS Nano* 2014** , 8, 1102–1120.

2. Jariwala, D. et al. Gate-Tunable Carbon Nanotube–MoS$_2$ Heterojunction p-n Diode. ***Proc. Natl. Acad. Sci. U.S.A.* 2013** , 110, 18076–18080.

9:20am **2D+AS+HI+NS+SS-ThM5 Graphene Transfer onto sub 1nm Al$_2$O$_3$/TiOPc/Graphene Gate Stacks**, ***Iljo Kwak***, *J.H. Park,* University of California at San Diego, *H.C.P. Movva,* University of Texas at Austin, *E.K. Kinder, H.L. Lu,* University of Notre Dame, *A.C. Kummel*, University of California at San Diego

A novel transfer method with chemically controlled interfacial adhesion is reported for the fabrication of novel logic devices. This method allows direct transfer onto gate stacks and eliminates the possibility of Au electrodes deposition could shorting the thin oxide prior to transfer. The top graphene layer was grown on a Cu layer on a SiO$_2$/Si substrate by CVD. Au electrodes were deposited on top of the graphene by e-beam evaporation. To transfer the graphene layer, PIB (Polyisobutylene) were drop cast on top of graphene prior to bonding of the Au/graphene/Cu to a PDMS (Poly-dimethylsiloxane) film. The PIB serves to moderate the adhesion between the PDMS (Poly-dimethylsiloxane) and the Au electrodes. The PDMS provides mechanical support. Afterwards, the PDMS/PIB/Au/graphene/Cu/SiO$_2$/Si stack was immersed in ammonium persulfate solution to dissolve the Cu, releasing the top graphene stack. The bottom gate stack was HOPG (highly ordered pyrolytic graphite) with a sub-nano Al$_2$O$_3$ film on a monolayer TiOPc(titanyl phthalocynine) film. The monolayer TiOPc was deposited via MBE at 100C and annealed to 250C to insure a monolayer film. The TiOPc acts as a nucleation layer for the oxide ALD. The Al$_2$O$_3$ layer was deposited by ALD using TMA (Trimethylaluminum) and H2O at 100 C. The PDMS/PIB/Au/Graphene stack was placed on the gate stack, and PDMS was removed. Using hexane solution, the rePIB layer was dissolved, leaving clean graphene surface. To measure the oxide characteristics, an AFM was converted into a capacitance meter. This measurement allows non-destructive probing of Au/graphene/Al2O3/TiOPc/graphene structure while conventional probe station could damage the oxide or electrodes.

9:40am **2D+AS+HI+NS+SS-ThM6 Effect of Monolayer Substrates on the Electronic Structure of Single-Layer MoS$_2$**, ***Alfredo Ramirez-Torres***, *D.T. Le, T.S. Rahman*, University of Central FLorida

We have performed first-principles calculations based on density functional theory (DFT) utilizing the optB88-vdW functional to study structural and electronic properties of a single layer of MoS2 deposited on single-layer substrates of hexagonal boron nitride (BN), graphene and silicene. All have a honeycomb structure; hence the formation of heterostructures is expected. Since the lattice mismatch between MoS2 and these substrates is large, we

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*** NSTD Student Award Finalist**

have considered different periodicities among layers to reduce as far as possible the incommensurability between lattices. Our results show that BN barely affects the electronic structure of isolate single-layer MoS2; the DFT gap remains proximately unchanged. Graphene and silicene severely modify the electronic structure introducing additional states within the optical gap. Adsorption on graphene produces that the system turns like a zero band gap semiconductor bringing the conduction bands of MoS2 down to the Fermi level of graphene. Adsorption on silicene shifts both valence and conduction bands of MoS2, towards the Fermi level of silicene, in addition to inducing a gap of about 50 meV in the silicene itself.

This work was partially supported by CONACYT (México) Postdoctoral Fellowship Program (number 204065) and DOE grant DE-FG02-07ER46354

11:00am **2D+AS+HI+NS+SS-ThM10 Ballistic Transport in Epitaxial Graphene Nanoribbons**, ***Walt de Heer***, Georgia Institute of Technology **INVITED**

Graphene nanoribbons are essential components in future graphene nanoelectronics. However, in typical nanoribbons produced from lithographically patterned exfoliated graphene, the charge carriers travel only about 10 nanometers between scattering events, resulting in minimum sheet resistances of about 1 kW In contrast 40 nm wide graphene nanoribbons that are epitaxially grown on silicon carbide are single channel room temperature ballistic conductors on greater than 10 µm length scale, similarly to metallic carbon nanotubes. This is equivalent to sheet resistances below 1W surpassing theoretical predictions for perfect graphene by at least an order of magnitude. In neutral graphene ribbons, we show that transport is dominated by two modes. One is ballistic and temperature independent; the other is thermally activated. Transport is protected from back-scattering, possibly reflecting ground state properties of neutral graphene. At room temperature the resistance of both modes abruptly increases non-linearly with increasing length, one at a length of 16 µm and the other at 160 nm. Besides their importance for fundamental science, since epitaxial graphene nanoribbons are readily produced by the thousands, their room temperature ballistic transport properties can be used in advanced nanoelectronics as well.

11:40am **2D+AS+HI+NS+SS-ThM12 Solution-Synthesized Graphene Nanoribbons**, ***Alexander Sinitskii***, University of Nebraska - Lincoln

In this talk I will discuss a recently developed bottom-up approach for gram quantities of narrow graphene nanoribbons that are less than 2 nm wide and have atomically precise armchair edges. These graphene nanoribbons have been characterized by a number of microscopic (STM, AFM, SEM, TEM) and spectroscopic (XPS, UPS/IPES, UV-vis-NIR, IR and Raman spectroscopy) techniques. The properties of graphene nanoribbons could be tuned by incorporation of nitrogen atoms in their edges. Narrow graphene nanoribbons have a large electronic bandgap, which makes them promising for applications in field-effect transistors with high on-off ratios, as well as bulk applications, including coatings, composites and photovoltaic devices.

12:00pm **2D+AS+HI+NS+SS-ThM13 Graphene Silicon Interfaces at the Two-Dimensional Limit**, ***Brian Kiraly***, *A.J. Mannix, M.C. Hersam,* Northwestern University, *N.P. Guisinger*, Argonne National Laboratory

Artificial van der Waals heterostructures have demonstrated both significant improvements of graphene's intrinsic properties and entirely new properties of their own. Early interest in these structures was based on nearly ideal carrier mobility in graphene on two-dimensional (2D) hexagonal boron nitride. Although exfoliation and reassembly of bulk vdW solids has yielded impressive initial results, this method inherently limits the geometry and constituent materials of these structures. Growth of 2D heterostructures has been demonstrated, but mainly limited to the prototypical graphene/hBN system. Adding new constituent materials, particularly those with electronic heterogeneity, to these 2D heterostructures allows them to be engineered with a variety of new properties.

We present the growth and characterization of interfaces between an atomically thin silicon layer and graphene. First, graphene is grown on Ag(111) via atomic carbon deposition at temperatures from 600°C -700°C. Following the growth of graphene, atomic silicon is evaporated on the graphene-covered Ag(111) substrate at 320°C-360°C. The resulting silicon growth results in facetted domains capped with a honeycomb lattice with periodicity 6.4 Å; Raman spectroscopy reveals peaks at 520 cm^{-1} and 900-1000 cm^{-1} thatcoincide precisely with bulk diamond cubic silicon, indicating these domains are comprised of *sp*^{3} bonded crystalline Si. These 2D sheets of silicon demonstrate both semiconducting character and a honeycomb lattice is attributed to a silver-based reconstruction of the Si(111) surface. The resulting silicon domains grow in two different configurations with respect to the dendritic graphene: (1) silicon domains appear to grow directly on the Ag(111) surface and terminate at the graphene boundaries. These in-plane interfaces are atomically-precise and clearly resolved via scanning tunneling microscopy. Electronically, the density of states of both isolated constituent materials persist to these interfaces within the resolution of the measurement, indicating little interaction at the border. (2) The silicon growth is observed *underneath* the existing graphene flakes. The vertically stacked silicon graphene domains are identified via atomically resolved imaging *through* the graphene domains at larger biases where graphene is transparent under STM. Furthermore, the vertical materials interfaces demonstrate distinct electronic signatures from either constituent material. The resulting interfaces represent atomically pristine interfaces between graphene and a *sp*^{3} bonded semiconducting Si film, demonstrating a significant step forward in the diversification of van der Waals heterostructures.

Atom Probe Tomography Focus Topic
Room: 301 - Session AP+AS+MC+NS+SS-ThM

APT Analysis of Semiconductors, Magnetic and Oxide Materials
Moderator: Paul Bagot, Oxford University, UK, Daniel Perea, Pacific Northwest National Laboratory

8:00am **AP+AS+MC+NS+SS-ThM1 A Vision for Atom Probe Tomography**, ***Thomas F. Kelly***, CAMECA Instruments Inc **INVITED**

Atom Probe Tomography has undergone revolutionary changes in the past two decades. It is tempting to think that these changes are likely to be followed by a period of adjustment and maturation but not continued innovation. However, there are still many active opportunities for development of atom probe tomography. Some of these new technologies are already upon us. There are recent major developments in data reconstruction, detector technology, data mining, and correlative microscopy. Furthermore, application areas are evolving at a rapid pace. The equipment needed to serve some applications will necessarily be developing alongside the more fundamental operating components of atom probes.

This talk with review some recent developments that are just emerging and will offer a vision for where the field is headed. Some of the unproven concepts needed to reach this vision will be highlighted.

8:40am **AP+AS+MC+NS+SS-ThM3 Interfaces in Semiconductors: Application to Photovoltaic Materials**, ***Oana Cojocaru-Mirédin***, Max Planck Institut fur Eisenforschung GmbH, Germany, *R. Würz*, Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg, Germany, *D. Raabe*, Max Planck Institut fur Eisenforschung GmbH, Germany **INVITED**

Cu(In,Ga)Se$_2$ (CIGS), Cu$_2$ZnSnSe$_4$ (CZTSe), and multicrystalline Si (mc-Si) solar cells possess a high efficiency [1], despite the polycrystalline structure of the absorber layer. One of the major factors controlling the cell efficiency is the diffusion of the impurities during the fabrication process into the absorber layer and to the p-n junction [2]. However, the interaction between the defects and the impurities at the internal interfaces is not completely understood. This is due to a lack of information on the local chemical changes across the internal interfaces at the nanoscale.

As a step towards a better understanding of the impurity redistribution at the internal interfaces, we have developed novel approaches of preparing site-specific atom probe specimens using combined focused ion beam (FIB), (scanning) transmission electron microscopy ((S)TEM) and electron backscattered diffraction (EBSD). These approaches allow selected GBs in polycrystalline CIGS, CZTSe and mc-Si layers to be studied by atom probe tomography (APT).

Several examples of correlative EBSD-TEM-APT (see Figure 1) and STEM-APT (see Figure 2) studies will be presented in this work. Using APT, segregation of impurities at the GBs was directly observed. APT data of various types of GBs will be presented and discussed with respect to the possible effects on the cell efficiency.

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[2] J. L. Shay, S. Wagner, H. M. Kasper, Appl. Phys. Lett. 27 (1975) 89, S. Yip and I. Shih, Proceedings of the 1st World Conference on Photovoltaic Energy Conversion (IEEE, Piscataway, 1994), p.210.

9:20am **AP+AS+MC+NS+SS-ThM5 Analysis of Discontinuous InGaN Quantum Wells by Correlated Atom Probe Tomography, Micro-Photoluminescence, and X-ray Diffraction**, *J. Riley, X. Ren,* Northwestern University*, D. Koleske,* Sandia National Laboratories*, **Lincoln Lauhon***, Northwestern University

In(x)Ga(1-x)N quantum wells are the foundation of solid-state lighting, with excellent quantum efficiencies despite high densities of defects. While there is as yet no universally accepted explanation for the high-efficiency, it is clear that carrier localization plays a role. Consistent with this picture, the quantum efficiencies of some samples can be improved by annealing and hydrogen gas to produce discontinuous quantum wells. However, the standard analysis of quantum well widths and composition by high-resolution x-ray diffraction is complicated by such complex morphologies. Specifically, the influence of surface roughness, and interfacial diffuseness, and planar continuity may be difficult to deconcolve. We will describe correlated analysis of continuous and discontinuous InGaN quantum wells by atom probe tomography, micro-photoluminescence, high-resolution x-ray diffraction, and atomic force microscopy. We find that precise composition profiles extracted from atom probe analysis enable refinement of x-ray diffraction peak fitting in the case of continuous quantum wells, and a better estimate of indium mole fraction and quantum well width. For discontinuous quantum wells, atom probe analysis enables simple models to be integrated into routine x-ray diffraction modeling to enable reliable extraction of indium mole fraction and better correlation with photoluminescence spectra. Correlation of atomic force microscopy tomographic images and micro-photoluminescence spectra over common sample areas, together with site-specific lift out techniques, will be presented to explore the surprising coexistence of high quantum efficiency and inhomogeneous broadening due to the complex underlying quantum well morphology.

9:40am **AP+AS+MC+NS+SS-ThM6 Atom Probe Tomography Characterization of Doped Epitaxial Oxide Multi-Layered Structures**, ***Nitesh Madaan****, A. Devaraj, Z. Xu, M.I. Nandasiri, S.A. Thevuthasan*, Pacific Northwest National Laboratory

Atom probe tomography is the state of the art 3D microscopy technique with sub-nanometer scale spatial resolution and ppm level mass sensitivity. For complex heterogeneous materials the accurate artifact-free reconstruction of collected data is quite a challenging task due to varying local evaporation fields leading to non-hemispherical evolution in the tip shape during the APT analysis. In this work we utilized laser assisted APT to analyze alternate multilayer oxide thin film structure of Samaria doped ceria (SDC) and Scandia stabilized zirconia (ScSZ), grown epitaxially on sapphire substrate, which is potentially useful for solid oxide fuel cells due to their high ionic conductivity. By analyzing the sample in different orientations (top-down, side-ways, and back-side) and comparing with dynamic tip shape evolution using level set simulations for similar geometries, an attempt was made to understand and decouple the APT evaporation artifacts from the real physical sample features. This study would help provide insights to improve the APT reconstruction process for complex multi-layered thin film materials.

11:00am **AP+AS+MC+NS+SS-ThM10 Atom Probe Tomography and Field Evaporation of Insulators and Semiconductors: Theoretical Issues**, ***Hans Kreuzer***, Dalhousie University, Canada **INVITED**

After reviewing the physics and chemistry in high electrostatic fields and summarizing the theoretical results for Atom Probe Tomography of metallic tips, we turn to the new challenges associated with insulators and semiconductors with regard to local fields inside and on the surface of such materials. The recent (theoretical) discovery that in high fields the band gap in these materials is drastically reduced to the point where at the evaporation field strength it vanishes will be crucial in our discussion.

11:40am **AP+AS+MC+NS+SS-ThM12 Atom Probe Tomography Investigation of the Microstructure of Multistage Annealed Nanocrystalline $SmCo_2Fe_2B$ Alloy with Enhanced Magnetic Properties**, ***Xiujuan Jiang****, A. Devaraj,* Pacific Northwest National Laboratory*, B. Balamurugan,* University of Nebraska-Lincoln*, J. Cui,* Pacific Northwest National Laboratory*, J. Shield*, University of Nebraska-Lincoln

Permanent magnets have garnered great research interest for energy applications. The microstructure and chemistry of a permanent magnet candidate—$SmCo_2Fe_2B$ melt-spun alloy—after multistage annealing was investigated using high resolution transmission electron microscopy (HRTEM) and atom probe tomography. The multistage annealing resulted in an increase in both the coercivity and magnetization as is desired for permanent magnets design. The presence of $Sm(Co,Fe)_4B$ (1:4:1) and $Sm_2(Co,Fe)_{17}B_x$ (2:17:x) magnetic phases were confirmed using both techniques. Fe_2B at a scale of ~ 5 nm was found by HRTEM precipitating within the 1:4:1 phase after the second-stage annealing. Ordering within the 2:17:x phase was directly identified both by the presence of antiphase boundaries observed by TEM and the interconnected isocomposition surface network found in 3D atom probe results in addition to radial distribution function analysis. These observed variations in the local chemistry after the secondary annealing were considered pivotal in improving the magnetic properties.

12:00pm **AP+AS+MC+NS+SS-ThM13 Detector Dead-time Effects on the Accurate Measurement of Boron in Atom Probe Tomography**, ***Frederick Meisenkothen***, National Institute of Standards and Technology (NIST)*, T.J. Prosa,* CAMECA Instruments Inc.*, E.B. Steel,* NIST*, R.P. Kolli*, University of Maryland, College Park

The atom probe tomography (APT) instrument uses a time-of-flight (TOF) mass spectrometer to identify ions that are field ionized and evaporated from the apex of a needle-like nano-tip specimen. A pulse event, either laser or voltage, is used to trigger field evaporation and to initiate the timing sequence for the mass spectrometer. Ideally, a single atom is field evaporated during a single pulse event. However, it is also common to have multi-hit detection events where more than one ion strikes the detector between pulses. For reasons not completely understood, some elements, such as boron, are prone to field evaporate in multi-hit detection events when compared to other elements, and a large fraction of the boron signal is reportedly lost during acquisition. Obtaining an improved understanding of the field evaporation behavior of boron at different concentration levels, in view of the limited ability of the detection system to resolve multi-hit detection events, may lead to new ways to compensate for the boron signal loss.

A nominally pure boron sample was chosen as a high boron concentration material while the boron implanted silicon, NIST-SRM2137, (1E15 atoms cm^{-2} retained dose) was chosen as the low boron concentration material. A dual-beam FIB/SEM instrument, with an *insitu* lift-out system, was used to prepare the APT specimen tips from the bulk materials. A laser pulsed LEAP 4000X Si* instrument was used to acquire APT data sets for each of the specimen tips. Custom software scripts were used to filter the data sets and extract the ion information associated with specific search criteria, e.g. event multiplicity, which is the number of ions within a given multi-hit event. Ion correlation analysis was used to graphically demonstrate the detector dead-time effect. In the present work, more than 60% of the detected boron signal resided within the multi-hit detection events, for both the high and low boron concentration samples.

* Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

Spectroscopic Ellipsometry Focus Topic
Room: 304 - Session EL+AS+EM+EN+SS-ThM

Spectroscopic Ellipsometry for Photovoltaics and Instrument Development

Moderator: Mariadriana Creatore, Eindhoven University of Technology, Netherlands, Tino Hofmann, University of Nebraska-Lincoln

8:00am **EL+AS+EM+EN+SS-ThM1 Spectroscopic Ellipsometry Characterization in the Photovoltaic Device Configuration**, ***Nikolas Podraza***, University of Toledo **INVITED**

Thin film large area photovoltaics (PV) are a maturing field, yet challenges remain in manufacturing and fundamental research. Even the simplest thin film PV devices consist of multiple layers of doped or undoped semiconductors, transparent conducting front contacts, and metal back contacts. Characteristics of each layer, along with the interfaces between layers, all have an impact upon device performance. Within each layer, the material may evolve with thickness or exhibit spatial non-uniformity. Furthermore, studies of each thin film material can be difficult, as fundamental property measurements on special substrates may not accurately represent the characteristics of the material in the final device configuration. Spectroscopic ellipsometry (SE) data, collected over the infrared to ultraviolet, is sensitive to layer thicknesses, interface formation, and surface roughness as well as the optical response of each component in the form of the complex dielectric function spectra ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) for samples deposited on arbitrary reflective substrates. Variations in ε for a given layer can be linked to order (amorphous vs. crystalline, grain size, crystal phase), composition, and characteristics of opto-electronic response (band gap, dc electrical properties). In situ real time SE (RTSE) is now often applied to study the growth evolution of component materials within device configurations for hydrogenated silicon (Si:H), cadmium telluride (CdTe), and copper indium gallium diselenide (CIGS) PV. This utilization of RTSE provides a means of monitoring layer characteristics as materials are being processed in the device structure and generates appropriate structural models for analysis of similar samples when only ex situ SE measurements are available. Appropriate structural models derived from RTSE have been applied to analyze ellipsometric spectra collected over 6 inch x 6 inch rigid substrates and assess the spatial uniformity in characteristics of each layer in the sample. These maps of optically derived material properties can be compared to electrical device performance (efficiency, open circuit voltage, short circuit current, fill factor) and used to guide PV optimization principles. The optical (ε) and structural (layer thickness) information gained from SE is input into quantum efficiency simulations for comparison with experimental PV device measurements. These comparisons are used to assess both opto-electronic performance of devices and validity of models used in SE data analysis as well as further guide device development by identifying sources of optical and electrical losses.

8:40am **EL+AS+EM+EN+SS-ThM3 Application of Pseudo-Bulk Approach in Ellipsometric Studies of Polycrystalline Photovoltaic Thin Films**, ***Sukgeun Choi***, National Renewable Energy Laboratory, *J. Li*, University of Toledo, *I. Repins*, National Renewable Energy Laboratory

Fundamental band gap is one of the key properties of semiconducting materials, which directly influences the functionality and performance of many photonic and photovoltaic (PV) devices. Photoluminescence (PL) and optical absorption spectroscopies are widely used to determine the band-gap energy E_g. For polycrystalline thin-film PV materials, however, it is often challenging to unambiguously interpret PL data owing to the presence of multiple peaks associated with various types of defect structures. To estimate E_g from optical absorption spectrum, on the other hand, a straight segment of the absorption coefficient curve needs to be chosen. But this selecting procedure is somewhat arbitrary, which leads to an inaccurate E_g value.

Spectroscopic ellipsometry (SE) accurately determines material's optical function spectra over a wide spectral range. For semiconductor thin-film structures, a multilayer analysis is generally used to extract the optical information from SE data. Although mainly surface overlayer artifacts need to be corrected for SE data well-above the band gap in the analysis, several contributions should be considered for those near (and below) the band gap, such as the optical characteristic of substrate, presence of interfacial layers, and finite thickness of film in addition to the artifacts from surface overlayers. As a result, the obtained optical function spectrum and E_g value become somewhat model dependent with an increased uncertainty.

To reduce complications in mathematical modeling of SE data and improve the accuracy of resulting near-band-gap optical function spectrum, we introduce the *pseudo-bulk* approach, where SE measurements are performed on thin films grown on macroscopically roughened substrate surface. The essence of this approach is in suppressing the reflection of probing light from the film/substrate interface and below. Thus, no thickness fringes appear in the SE data, despite the thin-film nature of sample, and the band-gap onset can be clearly observed with a post-growth chemo-mechanical polishing of the film surface. We apply the *pseudo-bulk* approach to study near-band-gap optical properties of $Cu_2ZnSnSe_4$ and related PV absorber materials. We present a non-monotonic temperature-dependence of E_g for $Cu_2ZnSnSe_4$ and the clear band-gap onset of Cu_2SnSe_3 at around 0.45 eV for the first time. SE results are explained by the results from the electronic structure calculations. The applicability and limit of this approach are also discussed.

9:00am **EL+AS+EM+EN+SS-ThM4 Real-Time and Through-the-Glass Mapping Spectroscopic Ellipsometry for Analysis and Optimization of CdS:O Window Layers of CdTe Superstrate Solar Cells**, ***Xinxuan Tan***, *R.W. Collins*, *P. Koirala*, *J. Li*, *N.J. Podraza*, University of Toledo

In-situ real-time spectroscopic ellipsometry (RT-SE) has been applied for the analysis of CdS:O films sputter deposited on c-Si substrates from a CdS target using different flow ratios of $O_2/(Ar+O_2)$ from 0 to 0.05. RT-SE studies of the CdS:O layers from the film side provide the complex dielectric function spectra of each the layers over a spectral range of 0.75 to 6.5 eV and its dependence on oxygen content in the material as deduced by energy dispersive X-ray spectroscopy (EDS). Ex-situ infrared ellipsometry of these samples enables extension of the dielectric function data to ~ 0.04 eV and provides information on free carrier conduction and chemical bonding in the material. In similar RT-SE studies, data acquired during the growth of CdS:O/CdTe layers on transparent conducting oxide (TCO) coated glass superstrates have been analyzed to determine the structural evolution of the layers in the configuration used for CdTe solar cells, with the CdS:O serving as an n-type window layer for the p-type CdTe absorber. The results of this analysis assist in the development of a realistic optical model for the multilayer structure of the solar cell. Using this optical model ex-situ through-the-glass spectroscopic ellipsometry (TG-SE) has been implemented toward the analysis of glass/(TCO-stack)/CdS:O/CdTe solar cells in the superstrate configuration.

For the solar cells, CdS:O layers with different oxygen contents were deposited on 15 cm x 15 cm TCO coated glass superstrates . A 16 x 16 array of dot cells each with an area of 0.125 cm^2 was fabricated on the superstrate in order to optimize efficiency improvements through combinatorial methods. Because the as-deposited superstrate/film-structure undergoes additional processing steps during device fabrication, three sets of TG-SE mapping data were acquired on (i) as-deposited, (ii) $CdCl_2$-treated (an activation step), and (iii) back-contact coated device structures. With an optical database that has been established for both as-deposited and $CdCl_2$ treated CdS:O, CdTe, and back contact materials, each of the TG-SE mapping data sets were analyzed based on an optical model deduced from RT-SE studies of the CdS:O and CdS:O/CdTe depositions. Thickness and compositional non-uniformity observed over the area by mapped by TG-SE enables correlations between solar cell performance and basic property parameters of the component layers including layer thicknesses and compositions. The resulting correlations provide a pathway to expedite solar cell optimization.

9:20am **EL+AS+EM+EN+SS-ThM5 Combined Optical Emission Spectroscopy and Spectroscopic Ellipsometry Collected During Thin Film Deposition**, ***Anna Barnes***, *M.M. Junda*, *N.J. Podraza*, University of Toledo

Plasma processes are commonly used to deposit thin film layers for a variety of optical, electronic, and coating applications. Two common processes widely used in the fabrication of thin films are physical vapor deposition (sputtering) and plasma enhanced chemical vapor deposition (PECVD). Non-contacting optical probes, such as spectroscopic ellipsometry (SE) and optical emission spectroscopy (OES), are particularly attractive techniques to study these deposition processes in situ during film growth. Connecting studies involving SE and OES offers the ability to observe and interpret the growth of thin films from plasma over time using variant parameters, though in different ways. Real time SE (RTSE) provides a means of monitoring the deposited material itself, while OES can be used to track variations in the plasma employed for the deposition. Tracking the time dependence of both film and plasma properties is desirable as variations in material properties resulting from changes in plasma conditions may impact the final device performance. In this particular study, we look at the growth evolution of semiconductor, transparent conducting oxide (TCO), and metal contact layers commonly used in thin film photovoltaic devices. Case studies involve undoped, n-type, and p-type hydrogenated amorphous silicon prepared by PECVD, as well as zinc oxide, indium tin oxide, and silver prepared by magnetron sputtering on either smooth test substrates (glass, crystal silicon wafers) or in the full device configuration. Variations in thin film structure (bulk layer thickness, surface roughness) and optical properties in the form of the complex dielectric function spectra ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) are obtained as a function of time by RTSE. Results from RTSE (ε, structure) are interpreted to determine order (grain size, amorphous vs. nanocrystalline), electronic transitions (band gap, free carrier absorption characteristics), and morphology evolution as appropriate for the given material layer. OES indicates the presence and relative strength of plasma emission peaks, which correspond to the species present in the plasma and their relative concentrations. Analysis of RTSE and OES data collected simultaneously is sought to identify links present between these plasma and film characteristics.

9:40am **EL+AS+EM+EN+SS-ThM6 Optical Insights into Graphene Functionalized by Atoms, Biomolecules and Metal Nanoparticles**, ***Maria Losurdo***, *M. Giangregorio*, *G.V. Bianco*, *P. Capezzuto*, *G. Bruno*, CNR-IMIP, Italy

New opportunities for energy production and storage, catalysis, biosensing, drug delivering and plasmonics are offered by graphene-based materials. In order to make all those applications viable technologies, it is mandatory to functionalize graphene for modulating reproducibly its properties and for better understanding the surface and interfacial electronic phenomena in graphene hybrids.

To this aim, this contribution discusses the optical properties measured by spectroscopic ellipsometry in the 0.6-6.5 eV of graphene functionalized by:

(1) the covalent attachment of hydrogen, nitrogen, oxygen, and fluorine atoms, which strongly affect the optical properties of graphene through a partial sp2-to-sp3 conversion of carbon.

(2) the non-covalent interaction with organic molecules such as porphyrins that interact with graphene through p-systems.

(3) a variety of metals nanoparticles, like Au, Ag, Ga, to create a versatile graphene-based platform for plasmonics in frequency range from the terahertz to the visible .

(4) plasmonic nanoparticles and subsequent proteins to create an electro-optical sensing graphene platform.

The graphene is grown by chemical vapor deposition (CVD) and transferred to glass substrates with coverage higher than 98%. This assures large area graphene samples that can easily accommodate the ellipsometric probing light spot avoiding uncontrolled effects due to undefined substrate/graphene boundaries. With the availability of high quality samples, effect of thickness and anisotropy, which have been debated for a while, are clarified.

Data on the real time monitoring of graphene optical properties by spectroscopic ellipsometry that allows for an unprecedented control over the degree of functionalization will also be presented.

The perspective of this work is twofold. From the fundamental point of view, in the investigated spectral range, the band structure of graphene has saddle van Hove-like singularities at the M points of the Brillouin zone, with possible excitonic effects. Focusing on the analysis of these singularities, many-body effects for all the graphene-derivates mentioned above are described.

From the technological point of view, it will be shown how the optical measurements can serves to clarify and explain the occurrence and stability of the doping of graphene by the various heteroatoms and molecules, the electron transfer between graphene and metals and molecules, and finally the sensitivity of the-graphene-platform in sensing gases and biomolecules.

Spectroscopic ellipsometry data of functionalized graphene are corroborated by Raman spectroscopy, microscopies and electrical characterizations.

11:00am **EL+AS+EM+EN+SS-ThM10 Enhanced Sensitivity to Surface-Normal Dielectric Function of Uniaxial-Anisotropic Materials via Attenuated Total Reflection Ellipsometry**, ***Thomas Tiwald***, J.A. Woollam Co., Inc., *J. VanDerslice, Z. Xiao, J.S. Huang*, University of Nebraska Lincoln

It is often difficult to determine the surface-normal dielectric functions of anisotropic materials, because to lack of sensitivity to optical properties out of the surface plane[1][2]. The primary cause is the large angle of refraction that occurs as the light enters from low index medium like air. In these circumstances, the penetrating light beam bends strongly towards surface normal, resulting in electric fields that are oriented primarily in the surface plane. This is a particular problem for absorbing films, since most of the light collected by the detector is reflected from the ambient/film interface. We use a total internal reflection method to enhance ellipsometric sensitivity to optical properties of uniaxial absorbing materials in the out-of-plane direction. This non-destructive technique is illustrated using a P3HT poly(3-hexylthiophene) film on fused silica, and the results are compared to the standard air/film/substrate method.

[1] D.E. Aspnes. *J. Opt. Soc. Am.*, **70**, 10, 1275 (1980).

[2] G. E. Jellison Jr. and J. S. Baba, *J. Opt. Soc. Am. A***23**, 2 468 (2006).

11:20am **EL+AS+EM+EN+SS-ThM11 Infrared to Ultraviolet Optical Properties of Gadolinium Gallium Garnet ($Gd_3Ga_5O_{12}$) and Bismuth Germanate ($Bi_4Ge_3O_{12}$) Single Crystals**, ***Kiran Ghimire***, *H. Haneef, N.J. Podraza*, University of Toledo

The optical properties of commercially available oxide single crystals gadolinium gallium garnet ($Gd_3Ga_5O_{12}$) and bismuth germanate ($Bi_4Ge_3O_{12}$) have been studied over a maximum spectral range of 0.034 to 6.5 eV by multiple spectroscopic ellipsometry and transmittance measurements, via a multichannel ellipsometer from the near infrared to ultraviolet, a Fourier transform infrared (FTIR) ellipsometer, and a spectrophotometer. Spectroscopic measurements from each instrument and over the respective spectral ranges have been analyzed differently yet yield optical properties over the full measured range. Near infrared to ultraviolet ellipsometric spectra are analyzed using a divided spectral range procedure whereby information below and above the band gap are fit to models with separate physically realistic parameterizations of the complex dielectric function spectra ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) that share the same structural parameters—surface roughness thickness in these cases. The surface roughness thicknesses are then fixed and direct numerical inversion is used to determine ε over the continuous spectral range. Analysis of transmittance and FTIR ellipsometric spectra also relies upon fixing surface roughness from near infrared to ultraviolet spectroscopic ellipsometry analysis and either direct numerical inversion or parametric models to determine ε. In the vicinity of the band gap, the absorption coefficient (α) obtained from ε is then combined with low values of ε obtained from transmittance below the absorption edge, where ellipsometry lacks sensitivity. The combined α from transmission and ellipsometry is used to determine the band gap of the materials. Unlike $Gd_3Ga_5O_{12}$, the band gap of the $Bi_4Ge_3O_{12}$ is sufficiently within the measured spectral range so critical point analysis has been performed on $Bi_4Ge_3O_{12}$ by extending the measured spectral range up to 6.5 eV, where the material was found to have additional critical points. FTIR ellipsometric spectra are analyzed with a parametric model combining Gaussian and Lorentzian broadened resonance features to represent modes attributed to chemical bonding and lattice vibrations. The results of these analysis procedures yield e from the infrared to ultraviolet, from which information on the band gap, electronic transitions, and vibrational modes are obtained.

11:40am **EL+AS+EM+EN+SS-ThM12 Cu surface reactions in hydrochloric solution probed on the atomic scale by polarization optical methods and STM**, ***Christoph Cobet***, *Gh. Barati, V. Solokha, K. Hingerl*, Johannes Kepler University, Austria

Electrochemical reactions on metal electrodes have been in the focus of many scientific studies and Cu is probably the most investigated example. Mainly, the interest on Cu is motivated by by questions concerning e.g. the corrosion behavior or the optimization of electro-polishing procedures. Classical electrochemical approaches contain usually a description of the occurring reaction products and concentrations. However, it is evident that a fundamental understanding also requires knowledge about the microscopic occurrence of the metal-electrolyte interface. Desirable is a fundamental knowledge as it is obtained already for surfaces in UHV. But unfortunately, most of the classical surface sensitive techniques cannot be applied in liquid environments. Thus it is not surprising that many fundamental issues in electrochemical reactions are still unsolved.

In our work we combine reflection anisotropy spectroscopy, spectroscopic ellipsometry, and a homemade electrochemical scanning tunneling microscope to study Cu single crystals in hydrochloric solutions. With these methods we enabled monitoring of the local appearance as well as the dynamics of interface transformations/reactions on the atomic scale. In particular it was possible to explain for the (110) surface in more detail the correlation of Faraday-current and structural transformation. Here, the Cl adsorption minimizes the surface energy by a formation of monoatomic steps parallel to the [001] direction which finally ends in a faceting of the surface. It turns out that characteristic redox peaks in cyclic voltammograms correlate with the stabilization of certain arrangements of these steps. The structures are formed first by Cu dissolution and at higher anodic potentials by rearrangement of Cu atoms in the surface. It is remarkable that the latter process compares nicely with oxide/chloride induced surface transformations which are observed in UHV. The comparison with the UHV results in turn is used to achieve a more comprehensive model for the processes in electrochemical environment.

Scanning Probe Microscopy Focus Topic
Room: 312 - Session SP+2D+AS+EM+MC+NS+SS-ThM

Probing Electronic and Transport Properties
Moderator: An-Ping Li, ORNL, Corentin Durand, ORNL

8:00am **SP+2D+AS+EM+MC+NS+SS-ThM1 Investigation of the Electronic and Structural Properties of Metal Free Naphthalocyanine Vapor Deposited on Au(111)**, ***Bryan Wiggins***, University of Chicago, *K.W. Hipps*, Washington State University

Naphthalocyanines (Ncs) are promising candidates for future components in electronic devices and applications. To maximize the efficiency of Nc devices, it is critical to understand their structural and electronic properties and how these are impacted by deposition methods. The formation of a metal free naphthalocyanine (H_2Nc) self-assembled monolayer on a Au(111) crystal was investigated by scanning tunneling microscopy under ultra-high-vacuum conditions at room temperature. A rigorous purification and processing procedure was developed to produce high purity, low defect, and well-ordered monolayers. High-resolution STM images reveal epitaxial growth of H_2Nc on Au(111) with the observed structure having a molecular spacing of 1.6 ± 0.05 nm, with molecules orientated slightly off (roughly 2.5°) the low density packing direction of Au(111). A commensurate structure having 4 molecules per unit cell and unit cell parameters of $A = 3.25 \pm 0.05$ nm, $B = 3.17 \pm 0.05$ nm, and $\alpha = 87.5 \pm 2°$ is proposed. Orbital-mediated tunneling spectroscopy was used to examine the electronic properties of individual molecules within the thin film. The first ionization potential and electron affinity of H_2Nc adsorbed on Au(111) were measured to be −0.68 ± 0.03 and 1.12 ± 0.02 eV, relative to the Fermi energy.

8:20am **SP+2D+AS+EM+MC+NS+SS-ThM2 The Fundamentals of Charge Transport at Oxide and Ferroelectric Interfaces**, ***Ramsey Kraya***, *L.Y. Kraya*, University of Pennsylvania

Here we investigate how charge transport properties at metal-semiconductor interfaces scale down to the nanoscale regime, comparing the properties to macroscopic interfaces and providing a perspective on what it means to device manufacturing. Strontium titanate - the prototypical oxide material - has been widely studied for applications in thermoelectrics, nanoelectronics, catalysis, and other uses, and behaves as an n-type semiconductor when doped. We investigated how charge transport is effected at interfaces to stronitium titanate under a wide range of conditions - by varying contact size, interface shape, dopant concentration, and surface structure and in various combinations. The results of the analysis have wide ranging implications, especially for ferroelectric oxide materials and serves as the basis for understanding and controlling switching effects - both polarization and oxygen migration based switching.

8:40am **SP+2D+AS+EM+MC+NS+SS-ThM3 Epitaxial Graphene on Nanostructured Silicon Carbide**, ***Phillip First***, Georgia Institute of Technology **INVITED**

Graphene grown epitaxially on silicon carbide conforms to nanofacetted step edges, even for step heights of many nanometers. The "sidewall" nanoribbons that result show astounding transport characteristics (~15 um ballistic length at room temperature), as demonstrated by others,[1] but the physical basis for these results is still not certain. In our STM measurements of sidewall nanoribbons, we find an extended 1D region with electronic structure much different than 2D graphene. Spectroscopic results on graphene near nanofacet corners indicate a strain gradient and a rapid change in the doping. Such strong gradients may be key to understanding the ballistic transport in this system. P

[1] J. Baringhaus, M. Ruan, F. Edler, A. Tejeda, M. Sicot, AminaTaleb-Ibrahimi, A.-P. Li, Z. Jiang, E. H. Conrad, C. Berger, C. Tegenkamp and W. A. de Heer, "Exceptional ballistic transport in epitaxial graphene nanoribbons," *Nature,* **506,** 349 (2014).

9:20am **SP+2D+AS+EM+MC+NS+SS-ThM5 Conductivity of Si(111) - 7 × 7: The Role of a Single Atomic Step**, *B. Martins,* University of Alberta and The National Institute for Nanotechnology, Canada*, M. Smeu, H. Guo,* McGill University, Canada*,* ***Robert Wolkow***, University of Alberta and The National Institute for Nanotechnology, Canada

The Si(111) - 7 × 7 surface is one of the most interesting semiconductor surfaces because of its

complex reconstruction and fascinating electronic properties. While it is known that the Si - 7 × 7 is

a conducting surface, the exact surface conductivity has eluded consensus for decades as measured

values differ by 7 orders of magnitude. Here we report a combined STM and transport measurement

with ultra-high spatial resolution and minimal interaction with the sample, and quantitatively determine the intrinsic conductivity of the Si - 7 × 7 surface. This is made possible by the capability of

measuring transport properties with or without a single atomic step between the measuring probes:

we found that even a single step can reduce the surface conductivity by two orders of magnitude.

Our first principles quantum transport calculations confirm and lend insight to the experimental

observation.

9:40am **SP+2D+AS+EM+MC+NS+SS-ThM6 Asymmetric Electron Transport Revealed at Monolayer-Bilayer Graphene Junctions by Atomic-Scale Scanning Tunneling Potentiometry**, *K. Clark, X. Zhang, J. Park,* Oak Ridge National Laboratory*, G. Gu,* University of Tennessee*, G. He, R.M. Feenstra,* Carnegie Mellon University*,* ***An-Ping Li***, Oak Ridge National Laboratory

The quest for novel two-dimensional (2D) materials has led to the discovery of hybrid heterostructures of graphene and other 2D atomic films [1]. These heterojunctions provide us fascinating playground for exploring electronic and transport properties in 2D materials. Even in graphene itself, there usually exist large amount of extended topological defects, such as grain boundaries, changes in layer thickness, and substrate steps, 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 present our recent study on an asymmetric electron transport upon bias polarity reversal at individual monolayer-bilayer (ML-BL) boundaries in epitaxial graphene on SiC (0001), revealed by multi-probe scanning tunneling potentiometry [2,3]. A greater voltage drop is observed when the current flows from monolayer to bilayer graphene than in the reverse direction, and the difference remains nearly unchanged when bias exceeds a threshold. A thermovoltage is measured across the boundary due to the thermopower difference between the two sides, which however is too small to account for the observed asymmetry. 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. Our theoretical analysis finds that Friedel charge oscillation opens a gap for electrons with wave vectors perpendicular to the boundary. The Friedel gaps are different on the monolayer and bilayer sides, which can shift under bias and lead to asymmetric transport upon reversing the bias polarity. A quantitative agreement is seen between experiment and theory on both the sign and the magnitude of the asymmetry.

1 "Heteroepitaxial Growth of Two-Dimensional Hexagonal Boron Nitride Templated by Graphene Edges", L. Liu, J. Park, D. A. Siegel, K. F. McCarty, K. W. Clark, W. Deng, L. Basile, J.-C. Idrobo, A.-P. Li, G. Gu, *Science***343**, 163-167 (2014).

2 "Spatially Resolved Mapping of Electrical Conductance around Individual Domain (Grain) Boundaries in Graphene", K. W. Clark, X.-G. Zhang, I. V. Vlassiouk, G. He, R. M. Feenstra, and A.-P. Li, *ACS Nano*. **7** (9), 7956-7966 (2013).

3 "Friedel Oscilation-Induced Energy Gap Manifested as Transport Asymmetric at Monolayer-Bilayer Graphene Boundaries", K. W. Clark, X.-G. Zhang, G. Gu, G. He, R. M. Feenstra, and A.-P. Li, *arXiv:* 1401.1796, *Physical Review X***4** (1), 011021 (2014).

11:00am **SP+2D+AS+EM+MC+NS+SS-ThM10 Defect-mediated Transport in CVD-grown Monolayer MoS$_2$**, ***Corentin Durand***, *J. Fowlkes,* Oak Ridge National Laboratory*, S. Najmaei, J. Lou,* Rice University*, A.P. Li*, Oak Ridge National Laboratory

Transition metal dichalcogenides like molybdenum disulphide (MoS$_2$) have attracted great interest as candidate to fill the need of 2 dimensional semiconductor materials. By controlling the thickness, the bandgap of MoS$_2$ thin films can be tuned from 1.2 eV (bulk material, indirect bandgap) to 1.8 eV (monolayer film, direct bandgap). Recently, researchers succeeded in growing monolayered MoS$_2$ by chemical vapor deposition (CVD) on silicon dioxide (SiO$_2$) substrate, showing the possibility of low cost scalable device fabrication. However, the mobility reported on exfoliated MoS$_2$ monolayers exceeds 200 cm^2.V^{-1}.s^{-1}, whereas the measurements realized on CVD growth MoS$_2$ monolayers reveal a mobility value that is usually 1-2 orders of magnitude lower. Here, we study the transport properties of CVD-grown monolayer on SiO$_2$/Si substrate. We directly measure the resistivity and the mobility of the material with a field-effect transistor architecture by using a cryogenic four-probe scanning tunneling microscope (STM), the Si substrate being used as back-gate. In order to ensure reliable electrical contacts, we fabricate platinum pads (4x4 µm^2) on individual MoS$_2$ crystal domains by using an electron-beam induced deposition technique. The combination of the STM scanners and a scanning electron microscope (SEM) enables us to connect the STM tips on those pads and thereby establish the contacts on this material without any subsequent lithography process, avoiding contaminations introduced by other technological steps. An electron hopping process in localized charge trapping states appears to dominate the transport behavior. We performed temperature-dependent measurements in the range of 82 K to 315 K which demonstrate a variable range hopping (VRH) transport with a very low mobility. Furthermore, the effects of electronic irradiation are examined by exposing the film to electron beam in the SEM in an ultra-high vacuum environment. We found that the irradiation process affect the mobility and also the carrier concentration of the material, with conductance showing a peculiar time-dependent relaxation behavior. It is suggested that the presence of defects such as vacancies and antisites create charge trapping states, leading to the low mobility. This is consistent with recent density functional theory calculations where these defects are shown to create localized gap states that can act as scattering centers and thereby reduce the mobility.

11:20am **SP+2D+AS+EM+MC+NS+SS-ThM11 Coherent One Dimensional Boundaries in Graphene and Hexagonal Boron Nitride Heterostructures**, ***Jewook Park***, Oak Ridge National Laboratory*, L. Liu,* The University of Tennessee Knoxville*, D.A. Siegel, K.F. McCarty,* Sandia National Laboratories*, L. Basile, J.-C. Idrobo, K. Clark,* ORNL*, W. Deng,* The Univ. of Tennessee Knoxville*, C.P. Durand,* ORNL*, G. Gu,* The Univ. of Tennessee Knoxville*, A.P. Li*, ORNL

The quest for novel two-dimensional (2D) materials has led to the discovery of hybrid heterostructures where graphene and other atomic layer films such as monolayer hexagonal boron nitride (hBN) form phase-separated domains or both materials grow epitaxially onto a common crystalline substrate. By implementing the concept of epitaxy to 2D space, we developed and applied a new growth technique to hybrid isostructural but electrically dissimilar materials, such as the 2D epitaxial growth of hBN templated by graphene edge [1]. Scanning tunneling microscopy and spectroscopy measurements revealed a single-atomic-layer, in-plane heterostructure between graphene and hBN, as well as an abrupt 1D zigzag oriented boundary. In addition, the dI/dV conductance map unveiled the 1D interfacial states that are extended along, but localized at the boundary. We investigated spatial and energetic distributions of 1D boundary states. Also, low-energy electron microscopy and micro low-energy electron diffraction confirmed the heterostructure at mesoscopic scale and established that the graphene edge solely determines the crystallography of the hBN regardless of underlying the Cu(100) lattice. The Z-contrast scanning transmission electron microscopy further indicates an atomically sharp interface with a transition width of ~0.5 nm. We suggest that the graphene-hBN epitaxial heterostructure provides an excellent platform to explore heteroepitaxy in 2D space, and the unique functionalities at the 1D interface. [1] Lei Liu *et al*. *Science***343** 163 (2014)

11:40am **SP+2D+AS+EM+MC+NS+SS-ThM12 Charge and Spin Density Waves in Quasi One-Dimensional Atomic Wires**, ***Herbert Pfnür***, Leibniz Universität, Germany **INVITED**

Although free one-dimensional (1D) objects should exist only at T=0, atomic single wires or arrays embedded into a two- or three-dimensional environment exist even at room temperature and above, since they are stabilized by lateral interactions. These interactions not only stabilize, but also strongly modify the properties of the wires. Their 2D or 3D coupling, however, does not generally prevent observation of 1D properties with their complex variety of instabilities. Furthermore, these coupling can result in special 1D behavior not predicted by standard theories either in 1D or 2D. I will show several examples how atomic wires and wire arrays grown by self-assembly on semiconducting surfaces of Si and Ge acting as insulating substrates can be used to study in detail fundamental aspects of low-dimensional physics, such as charge density waves [1] and Luttinger liquid behavior [2], partially under explicit control of the atomic structure. Due to the low symmetry in these structures, large Rashba-type spin-orbit coupling is expected to lift the spin degeneracy of the metal-induced surface states. In this context new types of spin order were proposed , e.g. for Au/Si(553) [3] and found to be consistent with experiment. As a further example, the Pb/Si(557) system close to monolayer coverage turned out to be an intruiging model system that demonstrates the whealth of phenomena to be expected in quasi-1D physics. Adsorbate induced electronic stabilization leads to (223) refacetting of the (557) surface, to opening of a band gap, to Fermi nesting normal to the steps [4]., and to the formation of a charge density wave. Rashba splitting is so large that it causes in-plane anti-ferromagnetic spin polarization along the steps with twice the step periodicity resulting in a combined spin-charge density wave. New superstructures are formed by an excess Pb coverage up to 0.1ML due to ordered step decoration indicating strong electron-electron correlation across steps. This leads to new long range ordered states and formation of a sequence of 1D charge density waves up to a concentration of 1.5 ML, but also, as very recent angular and spin resolved photoemission studies show, to new ordered spin states.

[1] T. Tanikawa et.al. Phys. Rev. Lett. 93, 016801 (2004).

[2] C. Blumenstein et.al. Nat. Phys. 7, 776 (2011).

[3] S.C. Erwin, F. J. Himpsel, Nature Communications 1, 58 (2010); J. Aulbach et al. Phys. Rev. Lett. 111, 137203 (2013)

[4] C. Tegenkamp, D. Lükermann, H. Pfnür, B. Slomski, G. Landolt H. Dil, Phys. Rev. Lett. 109,

266401 (2012).

Surface Science
Room: 309 - Session SS+TF-ThM

Organic Layers on Surfaces
Moderator: Edmund Seebauer, University of Illinois at Urbana Champaign

8:00am **SS+TF-ThM1 Orbital Tomography: Imaging the Wavefunctions of Adsorbed Molecules with Angle Resolved Photoemission**, ***Michael Ramsey***, University of Graz **INVITED**

Here it will be shown that the apparently complex angular distribution of valence band photoemission can be simply and quantitatively predicted from a Fourier transform of initial state wavefunctions. This will be demonstrated for a variety of orbitals of the proto-typical pi conjugated molecules pentacene, sexiphenyl and PTCDA on a number of substrate surfaces. For adsorbate monolayers it will be shown how this orbital tomography can be used to determine molecular geometries, unambiguously determine the orbital energy ordering, gain insight into the nature of the surface chemical bond and image the orbitals in real space.

8:40am **SS+TF-ThM3 Chemical Pathways for Surface Functionalization: From Surface-“Stapled” Nanostructures to Layered Materials**, ***Andrew Teplyakov***, University of Delaware

One of the important venues in designing novel interfaces and materials is based on the complementary functionalization of surfaces, modified molecules, and nanostructures, so that combining them would lead to layers and materials with novel chemical and physical properties. This presentation will focus of the molecular-level view of surface functionalization and extending the molecular approach to nanostructures and nanostructured layers with three-dimensional control. Classical organic reactions will be used to first build a nearly perfect layer of chemically functionalized nanoparticles on a flat surface and then the approach will be extended into the third dimension. The work will combine "click chemistry" with chemical functionalization approach and utilize surface analytical techniques including XPS, infrared spectroscopy, microscopic techniques combined with focused ion beam (FIB) sample preparation and will be complemented with the DFT studies. The spectroscopic techniques combined with DFT modeling will support the chemistry of deposition, while the electron microscopy techniques will confirm the growth of layered structures.

9:00am **SS+TF-ThM4 Observation and Trapping of Organic Reaction Intermediates for the Reaction of O(^{3}P) with Oligo(Phenylene Ethynylene) Thiolate Self Assembled Monolayers on Au(111)**, ***Wenxin Li***, *G. Langlois, N.A. Kautz, S.J. Sibener*, The University of Chicago

We have taken steps to develop a methodology for observing and trapping organic reaction intermediates by exposing well-ordered self assembled monolayers (SAM) to supersonic beams of atomic oxygen. The use of a SAM stabilizes highly energetic intermediates formed from bimolecular reactions at the interface due to rapid thermal equilibration with the SAM matrix. In this presentation we will discuss the elucidation of the mechanistic details for the fundamental reaction between O(^{3}P) and alkyne bonds by monitoring chemical and structural changes in an oligo(phenylene ethynylene) SAM reacting with O(^{3}P) under collision conditions having specified initial reaction orientation. Utilizing time-resolved reflection-absorption infrared spectroscopy (RAIRS) and scanning tunneling microscopy (STM) under ultrahigh vacuum conditions, we have directly observed electrophilic addition of O(^{3}P) onto the alkyne moieties, resulting in formation of a ketene intermediate via phenyl migration. Under single-collision conditions in the gas phase the vibrationally-excited ketene intermediate cleaves to release CO. In contrast to this, herein we have directly observed the formation of the condensed-phase stabilized singlet ketene by RAIRS. Moreover, we have also observed that the phenyl ring at the vacuum/film interface significantly cants towards the substrate plane as a result of this reaction. STM images of the SAM taken before and after O(^{3}P) exposure show an expansion of the ordered lattice resulting from formation of the new nonlinear molecular structures within the adsorbed film. This approach of using pre-oriented reactive molecules in ordered self assembled monolayers in combination with angle and velocity selected energetic reagents provides a general approach for probing the geometric constraints associated with the reaction dynamics for a wide range of chemical reactions.

9:40am **SS+TF-ThM6 Relative Stability of S-Au and Se-Au Bonding in Aromatic and Aliphatic Self-Assembled Monolayers – Exchange and Ion Desorption Experiments**, ***Jakub Ossowski***, *A. Noworolska,* Jagiellonian University, Poland, *S. Schuster,* University of Heidelberg, Germany, *J. Rysz,* Jagiellonian University, Poland, *A. Terfort,* University of Frankfurt, Germany, *M. Zharnikov,* University of Heidelberg, Germany, *P. Cyganik*, Jagiellonian University, Poland

Self-assembled monolayers (SAMs) are considered a model system in many areas on nanotechnology.[1] However, potential use of SAMs strongly depends on stability of their chemical bonding to the substrate. Most of the studies of SAMs have been performed using S-Au bonding.[1] More recently the Se-Au bonding is considered as an interesting alternative. However, as documented by the recent review,[2] there is still missing information which of these head group provides higher stability binding to the Au(111) substrate and whether or not this relative stability depends on the type of molecular backbone i.e. aliphatic or aromatic. A meaningful comparison of S-Au and Se-Au stability requires that respective molecules not only have the same carbon backbones, but also should form ordered structures with very similar molecular packing. Only under such conditions, not fulfilled by the most of previous studies, the contribution of the molecule-substrate bonding on the film stability can be elucidated. Following this idea, we will present a new data obtained for naphthalene based SAMs bound to the Au(111) substrate via S or Se atoms.[3] After presenting detailed microscopic (STM) and spectroscopic (XPS, NEXAFS) characterization of these SAMs, which exhibit very similar well-ordered structure, we will show results of two independent experiments probing the stability of their bond to the Au(111) substrate using an exchange method as well as ion-induced desorption (SIMS). We will compare these results with our previous exchange[4] and recent ion-desorption experiments[5] of aliphatic based systems. Irrespective of the type of molecular backbone our results clearly demonstrate much higher stability of the Se-Au bond as compared to the S-Au bond.

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11:00am **SS+TF-ThM10 CuPc:C_{60} Composite Films: From Sub–Monolayer to Multi-Layer Growth**, ***Taylor Stock**, J. Nogami*, University of Toronto, Canada

CuPc:C_{60} composite films of various compositions and thicknesses grown on the Cu(111) surface have been studied using room temperature scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS). At coverages below two monolayers (ML), phase segregated, ordered films, or well mixed, disordered films can be produced depending on the particular deposition sequence. This compositional variability is achieved by exploiting the differences in the relative strengths of the various molecule-substrate and molecule-molecule interaction forces. In thicker films, the CuPc-C_{60} intermolecular interaction dominates the growth, and for a range of concentrations these films are found to be well mixed, amorphous and thermally stable. These results provide a rationale for improvements that have been seen for organic light emitting diode (OLED) performance associated with C_{60} doping of CuPc molecular layers. [1]

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11:20am **SS+TF-ThM11 2D Co-Crystallization of Organic Ferroelectrics**, ***Axel Enders**, D.A. Kunkel, A. Sinitskii,* University of Nebraska-Lincoln, *S. Simpson,* University at Buffalo-SUNY, *J. Hooper,* Jagiellonian University, Poland, *E. Zurek*, University at Buffalo-SUNY

We will present an experimental study on the self-assembly and electronic properties of the organic ferroelectrics, croconic acid (CA), 3-hydroxyphenalenone (3-HPLN), and the related compound rhodizonic acid (RA) on crystalline metal surfaces. Importantly, the bond polarization of the selected organics is highly planar. This provides the foundation for the development of 2D polarization patterns by design, including rather complex ones like the honeycomb pattern recently discovered by our group [1]. What is remarkable about those honeycomb networks of CA, is that the interaction with the substrate is key to ferroelectric switching barriers. Also the structurally related 3-HPLN forms linear chains on surfaces that are expected to exhibit 2D polarization ordering within the plane of the 2D organic layer. The molecular arrangement can be manipulated through the use of the substrate and growth conditions, and we have also identified a new, chiral phase of hydrogen-bonded trimers of 3-HPLN. This surface-science approach was key to the first reported synthesis of RA crystalline structures [2]. Here we present an overview over the structural phases of select organic ferroelectrics on surfaces and how ordered 2D polarization states can emerge. Importantly, we discovered by co-deposition of CA and 3-HPLN that they form ordered 2D co-crystalline phases.). The structure of the resulting networks can be tuned by varying the relative concentration of the organics. Namely, for equal ratios of CA and 3-HPLN two polymorphs are observed, while for 2/1 CA/3-HPLN ratio, only a single structure is found. Transitions from CA rich structures to CA poor structures can be induced through weak annealing, in which the smaller CA desorbs before 3-HPLN. We expect that important ferroelectric properties of organic ferroelectrics, such as their ordering temperature and switching fields, can be manipulated through co-crystallization. We will highlight how surface science studies, specifically STM, can help accelerate co-crystal discovery.

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11:40am **SS+TF-ThM12 Phenol Adsorption on TiO_2(110): Evidence for Temperature Dependent Radical Formation**, ***Matthew Patterson**, M.F. DiTusa, C.A. Thibodeaux,* Louisiana State University*, RW. Hall,* Dominican University of California*, O. Kizilkaya, R.L. Kurtz, E.D. Poliakoff, P.T. Sprunger*, Louisiana State University

We have examined the electronic structure of phenol on rutile TiO_2(110) using angle resolved photoelectron spectroscopy (ARPES), electron energy loss spectroscopy (EELS), and density functional calculations on model phenoxy/TiO_2 clusters. Previous electron paramagnetic resonance studies have shown that exposure of titania powder to phenol at 250°C results in the formation of environmentally persistent free radicals(EPFRs), which have lifetimes on the order of dozens of hours and have been shown to exacerbate negative health effects caused by particulate matter. The proposed chemisorption model of radical formation from aromatic species on metal oxides involves electron transfer from the adsorbed organic to the metal oxide, locally reducing the oxide. Resonant ARPES shows direct evidence of charge transfer from high-temperature adsorbed phenol to electronic states of TiO_2 (110) usually associated with the accumulation of charge at surface oxygen vacancies, providing direct evidence of the hypothesized reduction mechanism. Electronic EELS reveals there is an associated decrease of phenol HOMO-LUMO gap. Electronic structure calculations using model phenoxy-TiO_2 clusters give insight into the changes induced in the occupied molecular orbitals of the chemisorbed phenoxyl radical. Results will be discussed in light of other metal oxide systems

12:00pm **SS+TF-ThM13 Adsorption behavior of Zinc Tetraphenylporphyrin Molecules on a Au(111) Surface**, ***Charles Ruggieri**, S. Rangan, R.A. Bartynski, E. Galoppini*, Rutgers, the State University of New Jersey

The interaction between Zinc Tetraphenylporphyrin (ZnTPP) molecules and the Au(111) surface is investigated using scanning tunnel microscopy (STM), from initial adsorption sites to monolayer organization, with a particular emphasis on its relation to the surface atomic structure and reorganization. When adsorbed at room temperature, ZnTPP molecules initially decorate step edges at low coverage. As the coverage approaches 0.5 monolayer (ML), ZnTPP molecules self-organize into islands of molecules in a rectangular array that is in registry with the underlying Au(111) lattice. The molecules are oriented with their macrocycles parallel to the surface, and form islands in areas delimited by herringbone reconstruction domain walls. As the coverage approaches one ML, the adsorption geometry of the self-organized molecular layer can be fully characterized with respect to the atomic structure of Au(111) surface atoms. Moreover, ZnTPP adsorption alters the Au(111) herringbone reconstruction domain size, most likely caused by anisotropic adsorbate-induced surface stress. However, when a monolayer is prepared from desorption of a ZnTPP multilayer, a different molecular organization is observed at the surface. It is proposed that this reconstruction is enabled by the particular reconstruction of the Au(111) surface. In this configuration, the domain size of the Au reconstruction is closer to that of clean Au, due to smaller adsorbate-induced surface stress.

2D Materials Focus Topic
Room: 310 - Session 2D+EM+MI+MN+NS+SS+TF-ThA

Novel Quantum Phenomena in 2D Materials
Moderator: Alexander Sinitskii, University of Nebraska-Lincoln

2:20pm **2D+EM+MI+MN+NS+SS+TF-ThA1 Optoelectronics of Two-Dimensional Semiconductors**, ***Xiaodong Xu***, University of Washington **INVITED**

Two dimensional transition metal dichalcogenides are a recent addition to the 2D electronic materials family. They have shown outstanding electrical and optical properties for new optoelectronic device concepts. In this talk, we will first discuss the unique interplay between spin, valley, and layer pseudospins in bilayer WSe_2. Such coupling effects lead to electrical control of spin states and optical generation of valley coherence through interlayer trions, where electrons and holes are localized in different layers. We will then talk about optoelectronic devices based on monolayer WSe_2, including p-n junctions as light emitting diodes and hybrid monolayer semiconductor/photonic crystal cavity devices. We will conclude the talk with a discussion of the optoelectronic properties of $MoSe_2$-WSe_2 heterostructures.

3:00pm **2D+EM+MI+MN+NS+SS+TF-ThA3 Theory of Graphene Transport Barriers in the Specular Limit**, ***Daniel Gunlycke***, *C.T. White*, Naval Research Laboratory

Offering room-temperature ballistic electron transport well over one micron, while being atomically thin and planar, graphene is undeniably a promising material for future nanoelectronic devices. Presently, however, switchable devices have normally low on-off ratios, a reflection of the challenge of selectively blocking electron and hole carriers from propagating across the graphene surface. This has stimulated a lot of research on different methods for making graphene nanoribbons that exhibit suitable band gaps. An alternative way to obtain a controllable gap takes advantage of resonant tunneling across a pair of transport barriers. For the latter approach, the key is to find a barrier that is fairly reflective but not so much as to effectively cut off all transport across it.

In this presentation, we present a model for straight transport barriers in graphene in the specular limit. Using the Lippmann-Schwinger equation, we obtain the wave function, from which we derive the reflection and transmission probabilities, as well as the local density of itinerant states. This local density of states exhibits fluctuations arising from quantum interference between incoming and outgoing matter waves that allow the transport properties of a barrier to be estimated without explicitly probing the current across the barrier. Our model is tested against exact multi-channel, tight-binding quantum transport calculations for graphene with weak local potentials, local strain, local adsorption, and a locally defective structure. As the model parameters are related to observable quantities, they could be obtained from theory and/or experiment, allowing the model to be adopted even when the precise details of the barrier are unknown.

3:20pm **2D+EM+MI+MN+NS+SS+TF-ThA4 Tip-induced Potential Confinement on Graphene in Scanning Tunneling Microscopy Measurement**, ***Yue Zhao***, *J. Chae, J.E. Wyrick,* NIST/CNST, *F.D. Natterer,* Ecole Polytechnique Fédérale de Lausanne (EPFL), France, *S. Jung,* Korea Research Institute of Standards and Science (KRISS), *A.F. Young, C.R. Dean, L. Wang, Y. Gao,* Columbia University, *J.N. Rodrigues,* Graphene Research Centre, NUS, Singapore, *K. Watanabe, T. Taniguchi,* National Institute for Materials Science (NIMS), Japan, *S. Adam,* Graphene Research Centre, NUS, Singapore, *J.C. Hone, K. Shepard, P. Kim,* Columbia University, *N.B. Zhitenev, J.A. Stroscio*, NIST/CNST

Graphene is a two-dimensional-electron-gas(2DEG) system with exposed surface, which allows scanning tunneling microscopy(STM) to investigate the electron-electron interaction associated with the Dirac nature on a local scale, with a variety of tuning knobs, such as carrier density, spatially varying disorder potential, and applied magnetic field. However, the electron-electron interaction in graphene is sensitive to the disorder details. Moreover, tip induced potential confinement can significantly complicate the interpretation of STM experiment. Utilizing a high mobility graphene device with low residual disorder, we can minimize the effect of local potential fluctuation, to better understand the role tip-induced potential plays in the measurement. We observed the emergency of large spectra gaps, modification to graphene Landau levels (LLs), and quantum dots with changing size due to the spatially inhomogeneous tip gating.

4:00pm **2D+EM+MI+MN+NS+SS+TF-ThA6 Topological Phase Transitions and Spin-orbit Density Waves**, ***Hugo Dil***, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland **INVITED**

In recent years systems where the spin-orbit interaction (SOI) is not just a perturbation but the main energy scale have received increasing attention. In combination with a broken inversion symmetry in the crystal structure or at interfaces, SOI will lift the spin degeneracy and induce a complex Fermi surfaces and spin textures with spin momentum locking [1,2]. Furthermore, the SOI can drive the system through a phase transition to a so-called topological insulator. Being an insulator in the bulk these systems are characterized by spin-polarized, topologically protected interface states.

After a short introduction to the role of topology in the band structure of solids I will give an overview of our main spin- and angle-resolved photoemission (SARPES) results on a variety of non-interacting topological insulators [3]. One of the questions is how the spin texture evolves around a topological transition. We explored the occurrence of spin polarized states around a SOI driven topological transition [4] and around a structure driven topological transition [5]. In both cases we observe spin-polarized precursor states, which indicate that although the topological transition is sharp, the response of the system is more gradual.

From a fundamental point of view the truly interesting aspect of non-trivial spin textures lies in their combination with other interactions. This can result in a variety of phenomena, cumulating in the creation of the elusive Majorana Fermion. An example of a combination of interactions is our recent verification with SARPES of SmB_6 as a topological Kondo insulator [6]. In topologically trivial systems, interactions can lead to the formation of a so-called spin-orbit density wave. I will show how the combination of a large spin-splitting and Fermi nesting leads to the formation of such a state and can explain the anisotropic behavior of Pb nanowires [7]. Furthermore, I will present our recent SARPES results for transition metal oxide surfaces where a subtle interplay between ferroelectricity and magnetic order results in the formation of a single spin-polarized energy contour. The occurrence of superconductivity in such systems could render it a 2D Majorana platform.

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4:40pm **2D+EM+MI+MN+NS+SS+TF-ThA8 The Symmetry Dependent Band Structure of MoS_2**, ***Duy Le***, University of Central Florida, *T. Komesu,* University of Nebraska-Lincoln, *Q. Ma,* University of California, Riverside, *E.F. Schwier, H. Iwasawa,* Hiroshima University, Japan, *M. Shimada,* Higashi-Hiroshima, Japan, *T.S. Rahman,* University of Central Florida, *L. Bartles,* University of California, Riverside, *P.A. Dowben*, University of Nebraska-Lincoln

We will present results of density functional theory (DFT) based calculations of symmetry dependent band structures of single crystal $MoS_2(0001)$ surface together with symmetry-polarized angle resolved photoemission spectroscopy (ARPES) derived experimental band structure. The good agreement of the DFT band structure with the experimentally derived bands with even and odd symmetries, attests to the reliability of the results. We performed ARPES at the Hiroshima Synchrotron, determining the MoS_2 band structure separately for both p-, and s-, polarized to distinguish even and odd symmetry, and the experimentally determined dispersion, in accordance with expectations and experimental confirmation of C_{3v} symmetry, argues in favor of an experimental band structure obtained from single domains. The comparison of theory and experiment provides strong indications that the bands at the top of the valence band are dominated by Mo 4d states. These states and indeed placement of the valence band can be perturbed by adsorbates. Indeed, we find that, under the effect of Na adsorption, the changing placement of the valence band structure of MoS_2 clearly indicate the Na atoms donate electrons to MoS_2 and that the Fermi energy level shifts as much as 0.5 eV with respect to the top of MoS_2's valance band. Surprisingly, Na adsorption does not perturb the MoS_2 band dispersion significantly. We will discuss these results in the light of those obtained for single layer MoS_2 for insights and clarity.

5:00pm **2D+EM+MI+MN+NS+SS+TF-ThA9 $CuIn_{III}P_2S_6$ - Room Temperature Layered Ferroelectric**, ***Alex Belianinov***, *P. Maksymovych,* Oak Ridge National Laboratory*, A. Dziaugys,* Vilnius University, Lithuania*, Q. He,* Oak Ridge National Laboratory*, E. Eliseev,* National Academy of Sciences of Ukraine*, A,. Borisevich,* Oak Ridge National Laboratory*, A. Morozovska,* NAS of Ukraine*, J. Banys,* Vilnius University, Lithuania*, Y. Vysochanskii,* Uzhgorod University, Ukraine*, S.V. Kalinin*, Oak Ridge National Laboratory

We have utilized ambient and Ultra High Vacuum Scanning Probe Microscopy tools to explore ferroelectric properties in cleaved 2D flakes of copper indium thiophosphate, $CuIn_{III}P_2S_6$ (CITP), and report on size effect and presently achievable limits of ferroelectric phase stability. CITP is an unusual example of a layered, anti-collinear, uncompensated, two-sublattice ferroelectric system. These are the only materials known to display "2-D" ferroelectric semiconductor behavior in a van-der-Waals crystal. The material exhibits a first-order phase transition of order–disorder type from the paraelectric to the ferrielectric phase at $T_c = 315$ K. Our observations suggest the presence of stable ferroelectric polarization as evidenced by domain structures, rewritable polarization, and hysteresis loops. These observations suggest that flakes above 100 nm have bulk-like polarization and domain structures, whereas below 50 nm polarization disappears. Furthermore, the materials have measurable ionic mobility, as evidenced both by macroscopic measurements and by formation of surface damage above tip bias of 4 V, likely due to copper reduction. We ascribe this behavior to well-known instability of polarization due to depolarization field, along with internal screening by mobile Cu ions, as suggested by their high ionic mobility.

Acknowledgement:

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5:20pm **2D+EM+MI+MN+NS+SS+TF-ThA10 Doping Efficiency and Mechanisms of Single and Randomly Stacked Bilayer Graphene by Iodine Adsorption**, ***Hokwon Kim***, *A. Tyurnina,* Univ. Grenoble Alpes/ CEA, LETI, France*, J.-F. Guillet, J.-P. Simonato, J. Dijon,* Univ. Grenoble Alpes/ CEA, LITEN, France*, D. Rouchon, D. Mariolle, N. Chevalier, O.J. Renault,* Univ. Grenoble Alpes/ CEA, LETI, France

The precise control of graphene's conductivity and work function is crucial in developing practical applications of graphene based electronics. In order to enhance the conductivity of graphene, we employed a simple doping method where graphene films produced by chemical vapor deposition and transferred onto SiO_2, Al_2O_3, and WO_3 substrates are p-doped with iodine vapor through physisorption at temperature of ~ 100 °C [1-3]. The work function values and iodine to carbon ratios of the one-layer (1L) and two-layer (2L) folded regions were analyzed by high spatial- and energy resolution X-ray photoelectron emission microscopy (XPEEM) on a *NanoESCA* instrument. After the iodine doping, the work function values were significantly increased up to ~0.4 eV and ~0.5 eV, respectively, for 1L and 2L graphene on SiO_2/Si. This higher degree of doping by iodine was corroborated by I $3d_{5/2}$ core level imaging of the same area where the 2L graphene exhibited significantly larger concentration of iodine (2 at. % versus 1 at. %) likely due to the intercalation of iodine at the inter-layer space.

The main iodine species identified by high resolution core level X-ray photoemission spectroscopy and Raman spectroscopy were I_3^- and I_5^- poly-iodide anionic complexes with slightly higher concentration of I_5^- in 2L than 1L graphene possibly due to different doping mechanisms. Temperature dependent ultra-high-vacuum, in-situ annealing of the doped films has demonstrated that most of iodine is removed above 300 °C for the both 1L and 2L regions, although a significant removal of iodine is observed for 2L graphene at temperature as low as 100 °C. Surprisingly, after the complete removal of iodine by annealing, the work function value did not return to the original one before the doping treatment and remained at a much higher value. This can be ascribed to the residual hydrocarbon contaminations interacting with the atomic defects within the graphene layer that lead to unintentional n-type doping in our samples[4].

Acknowledgement: The XPEEM and KFM measurements were performed at the Nanocharacterization Platform (PFNC).

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5:40pm **2D+EM+MI+MN+NS+SS+TF-ThA11 Use of XPS for Device Characterization**, *P. Aydogan, E.O. Polat, C. Kocabas,* ***Sefik Suzer***, Bilkent University, Turkey

A noncontact chemical and electrical measurement technique of XPS is utilized to investigate a number of devices made of graphene. The main objective of the technique is to trace chemical and location specific surface potential variations as shifts of the XPS peak positions under operating conditions. Devices consisting of graphene; (i) acting as a simple resistive element between two gold electrodes, (ii) a semiconducting sheet controlled by a back-gate, and (iii) between the source and the drain metal electrodes in a full transistor geometry, have been analyzed by recording the Au4f of the metal electrodes, the C1s of the graphene layer, and the O1s (or N1s) peaks of the silicon oxide (or nitride) of the substrate. The advantage of this technique is its ability to assess element specific surface electrical potentials of devices under operation based on the deviations of the core level peak positions in surface domains/structures. Detection of the variations in electrical potentials and especially their responses to various stimuli gives unprecedented information about the chemical nature as well as the location of structural and/or other types of defects as a result of doping, oxidation, reduction, etc.

Atom Probe Tomography Focus Topic
Room: 301 - Session AP+AS+EN+NS+SS-ThA

APT and FIM Analysis of Catalysts and Nanomaterials

Moderator: David Diercks, Colorado School of Mines, David Larson, CAMECA Instruments Inc.

2:20pm **AP+AS+EN+NS+SS-ThA1 *In Situ* Study of Gas - Solid Reactions via Environmental APT**, ***Krishna Rajan***, Iowa State University **INVITED**

In this presentation we describe the design and examples of applications of the use of an environmental cell integrated into a LEAP atom probe. The use of such a cell helps to open up the field of in-situ gas-solid reactions by permitting one to study surface and near surface reactions which are closer to ambient conditions than is possible in traditional surfaces science studies. The implications for this experimental approach in the context of the study of catalysts and nanomaterials are discussed.

3:00pm **AP+AS+EN+NS+SS-ThA3 Propagation of Chemical Waves: A Field Emission Microscopy Study**, ***Cédric Barroo***, *Y. De Decker, N. Kruse, T. Visart de Bocarmé*, Université Libre de Bruxelles, Belgium

Thecatalytic hydrogenation of NO_2 over platinum field emitter tips has been investigated by means of field emission techniques. Field emission microscopy (FEM), as well as field ion microscopy (FIM), has been proved to be an efficient method to study the dynamics of catalytic reactions occurring at the surface of a nanosized metal tip, which represents a good model of a single catalytic nanoparticle. These studies are performed during the ongoing reaction which is imaged in real time and space. Nanoscale resolution allows for a local indication of the instantaneous surface composition.

The presence of adsorbates modifies the value of the local work function. These variations are expressed by modulations of the brightness of field emission patterns. A qualitative investigation of the local surface composition is then possible as function of time.

The microscope is run as an open nanoreactor, ensuring that the system is kept far from thermodynamic equilibrium. Under these conditions, chemical reactions can induce time and space symmetry breaking of the composition of a system, for which periodic oscillations and target patterns are well-known examples.

Self-sustained periodic oscillations have been reported for the NO_2 reduction. By increasing the time resolution of the system, it is now possible to study the emergence of these oscillations and to observe the propagation of chemical waves at the nanoscale, on a single facet of a nanocrystal. The velocity of wave propagation is estimated to be in the µm/s range, which is in accordance with previous studies of catalytic reaction at the mesoscale.

3:20pm **AP+AS+EN+NS+SS-ThA4 3D Nanoscale Chemical/Structure Analysis in Mineral Carbon Sequestration Study using Atom Probe Tomography**, ***Jia Liu**, D.E. Perea, R.J. Colby, L. Kovarik, B. Arey, O. Qafoku, A. Felmy*, Pacific Northwest National Laboratory

Mineral carbon sequestration is one of the important means to store CO_2 in order to mitigate the environmental concern regarding ever-growing anthropogenic CO_2 emissions. Olivines, X_2SiO_4 where X = Mg and Fe, hold promise as potential media to sequester carbon due to its broad availability in basalt deposits and reactivity to form stable metal carbonates. Site-specific reactivity of olivine with supercritical CO_2 is of great interest in understanding the fundamental elementary reaction mechanisms, where the presence of impurities within the bulk mineral may affect reaction kinetics. A combination of atom probe tomography (APT) and scanning transmission electron microscopy (STEM) is being used to map the complex composition and nanoscale structure across various site-specific regions. APT analysis of unreacted natural fayalite indicates the presence of 2-3-nm-thick hydrated iron oxide layers. In addition, Na impurities were found to concentrate within the hydrated layers while Mg and Mn were depleted from these regions. With the ability of APT to detect the chemical/structural heterogeneity at nanometer-scale, we find that APT will provide a means to correlate with ongoing experimental reaction studies and also provide guidance into models of the heterogeneous phase formation and reaction rates at precisely defined interfaces within minerals.

4:00pm **AP+AS+EN+NS+SS-ThA6 Catalyst Nanomaterials Analysis via Atom Probe Tomography**, *P.A.J. Bagot,* Oxford University, UK, *Q. Yang,* University of Oxford, UK, *K. Kruska,* Pacific Northwest National Laboratory, *D. Haley,* University of Oxford, UK, *E. Marceau, X. Carrier,* Université Pierre et Marie Curie, France, ***Michael Moody***, University of Oxford, UK **INVITED**

Heterogeneous catalytic materials play an increasingly critical, yet largely unnoticed, role underpinning countless modern technologies. Their active components are generally transition group metals, each of which offers different catalytic properties in terms of selectivity, yield and stability under demanding operating conditions. The need to develop more efficient catalysts that meet industrial demands and comply with environmental legislation targets requires better understanding how different catalysts may alter at the atomic scale in terms of structure or surface composition under their respective operating environments. Further, many catalysts take the form of nanoparticles, the performance of which can be strongly correlated to size, shape, chemistry and structure. However, discerning the nature of nanoparticles scale poses significant challenges to conventional microscopy.

Recently, atom probe tomography (APT) techniques have been developed to provide unique insight into the behaviour of catalyst alloys subject to conditions like those experienced in service [1–3]. This study is aimed at more accurate and insightful analyses comprising unique 3D atomistic descriptions of the evolving alloy nanostructure which can then be correlated to catalyst performance. Here, APT results are presented for characterization of oxidation-induced segregation in a Pt-Pd-Rh gauze and Fe-Ni alloy catalysts. Progress in the development of new approaches for the analysis of nanoparticles via APT is also presented.

[1] T. Li et al., Atomic engineering of platinum alloy surfaces. Ultramicroscopy 132, 205 (2013).

[2] T. Li et al., Atomic Imaging of Carbon-Supported Pt, Pt/Co, and Ir@Pt Nanocatalysts by Atom-Probe Tomography. ACS Catalysis 4, 695 (2014).

[3] P. Felfer et al, Long-Chain Terminal Alcohols through Catalytic CO Hydrogenation. Journal of the American Chemical Society 135, 7114 (2013).

Spectroscopic Ellipsometry Focus Topic
Room: 304 - Session EL+AS+EM+MC+SS-ThA

Optical Characterization of Nanostructures and Metamaterials

Moderator: David Aspnes, North Carolina State University, Mathias Schubert, University of Nebraska-Lincoln

2:20pm **EL+AS+EM+MC+SS-ThA1 The Optical Properties of Metallic Nanostructures**, ***Bruno Gompf***, Universität Stuttgart, Germany **INVITED**

The entire optical response of a homogenous reciprocal sample can be characterized by eight basic physical properties: mean absorption, mean refraction, circular birefringence and circular dichroism, linear birefringence and linear dichroism (0°, 90°), linear birefringence and linear dichroism (-+45°). Always two out of the three main birefringence-dichroism pairs (basic anisotropies) are sufficient to jump from any point of the Poincare-sphere to any other. A common example is the Soleil-Babinet compensator. This implies that always two of the basic anisotropies generate artificial signals of the third [1]. Therefore even for perfect crystals it is hard to judge, what optical property lead to an observed polarization change.

In the case of inhomogeneous materials the permittivity additionally becomes k-dependent $\varepsilon_{ij}(\omega, k)$; it exhibits spatial dispersion. For most artificial nanostructures, dubbed metamaterials, the building blocks are in the range $l/10 < P < l/2$. During the last couple of years it has become clear that in general it is not possible for these kinds of materials to define *effective* optical parameters, which are independent of the angle of incidence of the probing light. There optical response is intrinsically k-dependent.

With Mueller-matrix spectroscopic ellipsometry the entire optical response of artificial nanostructures can be characterized. For this the Mueller-matrix elements $m_{ij}(\theta, \alpha, \omega)$, which depends on the angle of incidence q, the azimuth orientation a and the energy, had to be measured over the complete angular and a wide frequency range. Visualizing the results in polar contour plots enables a detailed analysis of how nanostructures influence the polarization state of light [2-4]. Most importantly, immediate experimental evidence is obtained for deviations from pure dielectric behaviour; i.e. the optical response cannot be explained by an effective $\varepsilon_{i,j}(\omega)$ alone but requires spatial dispersion.

In the talk the entire optical response of a some artificial nanostructures will be presented and some generalizations will be discussed, when spatial dispersion becomes important and how it can be distinguished from other optical properties leading to a mixing of polarization states, like birefringence and optical activity.

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[2] B. Gompf, J. Braun, T. Weiss, H. Giessen, M. Dressel, U. Huebner, Phys.Rev.Lett. **106**,

185501 (2011).

[3] B.Gompf, B. Krausz, B. Frank, M. Dressel, Phys.Rev.B. **86**, 075462 (2012).

[4] A. Berrier, B. Gompf, Liwei Fu, T. Weiss, H. Schweizer, Phys.Rev.B. in print

3:00pm **EL+AS+EM+MC+SS-ThA3 Mueller Matrix Ellipsometry As a Powerful Tool for Nanoimprinted Grating Structure Metrology**, ***Xiuguo Chen**, C.W. Zhang, S.Y. Liu*, Huazhong University of Science and Technology, China

Compared with conventional ellipsometric scatterometry, which only obtains two ellipsometric angles, Mueller matrix ellipsometry (MME, sometimes also referred to as Mueller matrix polarimetry) based scatterometry can provide up to 16 quantities of a 4 by 4 Mueller matrix in each measurement. Consequently, MME can acquire much more useful information about the sample and thereby can achieve better measurement sensitivity and accuracy. In this talk, we will demonstrate MME as a powerful tool for nanoimprinted grating structure metrology. We will show that MME-based scatterometry at least has the following three aspects of advantages over conventional ellipsometric scatterometry.

(1) More accurate characterization of line width, line height, sidewall angle, and residual layer thickness of nanoimprinted grating structures can be achieved by performing MME measurements in the optimal configuration. In contrast, conventional ellipsometric scatterometry can only be conducted in the planar diffraction configuration, i.e., with the plane of incidence perpendicular to grating lines, which is not necessarily the optimal measurement configuration for nanostructures in general.

(2) Not only further improvement in the measurement accuracy and fitting performance can be achieved, but also the residual layer thickness variation over the illumination spot can be directly determined by incorporating depolarization effects into the interpretation of measured data. The depolarization effects, which are demonstrated to be mainly induced by the finite bandwidth and numerical aperture (NA) of the instrument, as well as the residual layer thickness variation of the nanoimprinted grating structures, can be only handled by MME.

(3) Conventional ellipsometric scatterometry has difficulties measuring asymmetric grating structure due to the lack of capability of distinguishing the direction of profile asymmetry. In contrast, MME not only has good sensitivity to both the magnitude and direction of profile asymmetry, but also can be applied to accurately characterize asymmetric nanoimprinted gratings by fully exploiting the rich information hidden in the measured Mueller matrices.

3:20pm **EL+AS+EM+MC+SS-ThA4 Vector Magneto-Optical Generalized Ellipsometry on Sculptured Thin Films with Forward Calculated Uniaxial Response Simulation**, ***Chad Briley***, *T. Hofmann,* University of Nebraska-Lincoln, *D. Schmidt,* National University of Singapore, *E. Schubert, M. Schubert*, University of Nebraska-Lincoln

We present the vector magneto-optical generalized ellipsometric (VMOGE) response and forward calculated simulations of ferromagnetic slanted columnar thin films. Directional hysteresis magnetization scans were performed with an octu-pole vector magnet at room temperature on slanted columnar thin film samples of permalloy grown by glancing angle deposition passivated by an atomic layer deposited Al2O3 conformal coating. Model analyses of the measured Mueller matrix ellipsometric data through a point-by-point best match model process determines the magneto-optical (MO) dielectric tensor. Three dimensional rendering of the anti-symmetric off-diagonal elements of the MO dielectric tensor reveal a uniaxial magnetic response of the thin film along the long axis of the columns. The magnetic response was subsequently modelled by a best match model process with uniaxial hysteretic response governed by the shape induced anisotropy from the physical geometry and orientation of the nano-columns. By using model parameters for normalized saturation ||Ms||=1, coercivity ||Hc||=50 mT, and remenance ||Mr||=0.9999*||Ms|| the forward calculated magnetic simulations described the observed magneto-optical response for all measured orientations of the nano-columns with respect to all magnetizing field directions generated by the vector magnet.

1) D. Schmidt, C. Briley, E. Schubert, and M. Schubert Appl. Phys. Lett. 102, 123109 (2013)

4:00pm **EL+AS+EM+MC+SS-ThA6 *In Situ* Generalized Ellipsometry Characterization of Silicon Nanostructures during Lithium-ion Intercalation**, ***Derek Sekora***, *R.Y. Lai, T. Hofmann, M. Schubert, E. Schubert*, University of Nebraska-Lincoln

Nanostructured silicon has emerged as a leading candidate for improved lithium-ion battery electrode design. The combined highly accessible surface area and nanoscale spacing for volumetric lattice expansion of nanostructured thin films have shown improved cycle lifetime over bulk-like silicon films. Additionally, ultra-thin passivation layers have been reported to increase the longevity and stability of silicon thin film electrodes. Very little *in-situ* information has been reported on silicon films during the complicated lithiation process. Furthermore, what information available has been limited to the study of bulk-like thin films. The advantageous geometry of glancing angle deposited (GLAD) thin films allows for the strain from lithiation to affect individual nanostructures in comparison to the bulk response. For this reason, alumina passivated GLAD silicon films were grown for use as working electrodes in half cell electrochemical experiments.

The spatially coherent silicon GLAD nanostructures have intrinsic biaxial optical properties. Therefore, generalized ellipsometry was employed to investigate the silicon film's physical response to lithium intercalation during an electrochemical cyclic voltammagram cycled against pure lithium metal in a conductive anhydrous electrolyte solution. *In-situ* ellipsometric monitoring of directional optical constant changes determined by the homogeneous biaxial layer approach are presented. The optical response expresses a morphologic conversion from a highly anisotropic film to a pseudo-isotropic lithium concentrated form and subsequently, its return to the original anisotropic state. The ability to nondestructively monitor complex nanostructured thin films during lithium-ion processes provides new avenues for high storage battery electrode design.

4:20pm **EL+AS+EM+MC+SS-ThA7 Characterization of SiO_2 Nanoparticle Layers on a Glass Substrate by Spectroscopic Imaging Ellipsometry and AFM**, ***Peter H. Thiesen***, Accurion GmbH, Germany, *G. Hearn,* Accurion Inc., *C. Röling*, Accurion GmbH, Germany

The well-directed organization of nanoparticles is of increasing technical and scientific interest. One approach is the organization of nanoparticles at the air/water interface for applications, like producing 2D colloidal crystals or nanowires. For example, Gil et al. (2007) monitored the formation of 2D colloidal crystals by Langmuir–Blodgett technique. They used Brewster angle microscopy to observe the film quality. Zang et al. (2009) have also studied silica nanoparticle layers at the air/water interface by multiple angle of incidence ellipsometry. For data interpretation, a two-layer model was introduced. With this model, the radius of interfacial aggregates and the contact angle of the nanoparticle surface at the air/water interface were obtained.

In this paper different line shaped pattern of SiO_2 nanoparticles were characterized by spectroscopic imaging ellipsometry in the wavelength range between 360 and 1000 nm and by AFM. The samples were provided by the research group of Professor Y. Mori, Doshisha University, Japan.

The work shows the unique capability of imaging ellipsometry in characterizing patterned surfaces. We started with a pre inspection of the surface by imaging ellipsometric contrast microscopy. Tiny regions of interest (ROIs) were placed on interesting areas like on different steps of the stripes and Delta and Psi spectra were recorded. The next step in characterization was the mapping of Delta and Psi with pixel resolution of the detector. The same samples were also characterized with an AFM. The results optical modelling are in good agreement with the results of the scanning method.

A. Gil, M. Vaupel, F. Guitiana, D. Möbius (2007) *Journal of Materials Chemistry* **17**: 2434–2439.

D. Zang, A. Stocco, D. Langevin, B. Weib, B.P. Brinks (2009) *Phys. Chem. Chem. Phys.***11**: 9522–9529.

5:00pm **EL+AS+EM+MC+SS-ThA9 Dielectric Tensor Model for Inter Landau-level Transitions in Highly Oriented Pyrolytic Graphite and Epitaxial Graphene – Symmetry Properties, Energy Conservation and Plasma Coupling**, ***Philipp Kühne***, Linköping University, Sweden, *T. Hofmann, M. Schubert,* University of Nebraska-Lincoln, *C.M. Herzinger,* J.A. Woollam Co., Inc., *V. Darakchieva*, Linköping University, Sweden

We report on polarization sensitive, magneto-optic, reflection-type Landau level (LL) spectroscopy at low temperatures by using the integrated optical Hall effect instrument[1] in the mid-infrared spectral range (600 – 4000 cm^{-1}) on highly oriented pyrolytic graphite (HOPG) and epitaxial graphene grown on C-face silicon carbide by thermal decomposition. In both sample systems we observe a multitude of inter-LL transitions. Inter-LL transitions in HOPG possess polarization mode mixing polarization selection rules characteristics, while polarization mode conserving and polarization mode mixing inter-LL transitions are observed in epitaxial graphene which can be assigned to single- and Bernal stacked (ABA) multi-layer graphene, respectively.[2] We present a new dielectric tensor model for inter-LL transitions which explains all experimentally observed line-shapes. For inter-LL transitions in multi-layer graphene and HOPG we employ this new model together with energy conservation considerations, to show that these polarization mode mixing inter-LL transitions couple with a free charge carrier plasma. Finally, inter-LL transition energy parameters are determined and discussed.

[1]) P. Kühne, et. al., Rev. Sci. Instrum., accepted (2014)

[2]) P. Kühne, et. al., Phys. Rev. Lett. **111**, 077402 (2013)

5:20pm **EL+AS+EM+MC+SS-ThA10 Characterization of Exfoliated 2D Nano Materials with Imaging Spectroscopic Ellipsometry**, *P.H. Thiesen,* Accurion GmbH, Germany, ***Greg Hearn***, Accurion Inc., *B. Miller,* Technische Universität München, Germany, *C. Röling,* Accurion GmbH, Germany, *U. Wurstbauer,* Columbia University, *E. Parzinger, A.W. Holleitner, U. Wurstbauer*, Technische Universität München, Germany

In the initial period of graphene research, the issue was to identify and characterize crystallites of microscopic scale. Imaging ellipsometry is a nondestructive optical method in thin film metrology with a lateral resolution down to 1 µm. In a number of papers, Imaging ellipsometry has been applied to characterize graphene flakes of few micrometer size. Ellipsometric contrast micrographs, delta and Psi maps as well as wavelength spectra [1],[2] and single layer steps in multilayer graphene/graphite stacks [3] have been reported.

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. Delta and Psi Spectra of MoS_2 monolayers as well as maps of the ellipsometric angles will be presented. The practical aspect of single layer identification will be addressed and the capability of ellipsometric contrast micrographs as a fast tool for single layer identification will be demonstrated.

An additional focus will be on the modelling of the optical properties of 2D nanomaterials.

[1] Wurstbauer et al., Appl. Phys. Lett. 97, 231901 (2010)

[2] Matkovic et al. J. Appl. Phys. 112, 123523 (2012)

[3] Albrektsen O. J. OF Appl. Phys. 111, 064305 (2012)

Scanning Probe Microscopy Focus Topic
Room: 312 - Session SP+AS+BI+NS+SS-ThA

Probing Chemical Reactions at the Nanoscale
Moderator: Carl Ventrice, Jr., University at Albany-SUNY, Jun Nogami, University of Toronto, Canada

2:20pm **SP+AS+BI+NS+SS-ThA1 Surface Structures of Catalysts in Reactive Environments with Scanning Tunneling Microscopy**, ***Franklin (Feng) Tao***, *L.T. Nguyen*, University of Notre Dame **INVITED**

Structure and chemistry of catalysts under a reaction condition or during catalysis are the key factors for understanding heterogeneous catalysis. Advance in ambient pressure photoelectron spectroscopy has taken place over the last decades, which can track surface chemistry of catalysts in gas environment of Torr or even tens of Torr pressure range. Environmental TEM has been developed for studying structures of catalysts while they are in a gas or liquid phase. In terms of environmental TEM, images at a pressure up to bars have been obtained although 1-10 Torr to one bar is the typical pressure range of in-situ studies of catalysts by E-TEM. Compared to structural and chemical information of catalyst particles offered from environmental TEM, packing of adsorbed molecules on a catalyst surface and arrangement of catalyst atoms of catalyst surface are complementary for the structure information provided by environmental TEM. High pressure scanning tunneling microscopy (HP-STM) is the most appropriate technique to achieve these pieces of important information. With the HP-STM the structures of surfaces of model catalysts under a reaction condition or during catalysis can be visualized. Surface structures of catalysts only formed under a reaction condition or during catalysis can be tracked. Such information is significant for understanding catalysis performed at solid-gas interfaces.

In this talk, I will present the historical development of HP-STM. Then, I will review the pressure-dependent packing of chemisorbed molecules; one type of pressure dependence is the change of packing of adsorbates from site-specific binding in UHV or a gas phase with a low pressure to non-specific binding in a gas phase at a relatively high pressure; the other type is a switch from one specific binding site to another specific binding site along the increase of the pressure of gas phase of the reactant. In addition, restructuring of a catalyst surface is another consequence of the increase of the gas phase pressure. The threshold pressure at which a restructuring is performed depends on the original surface structure and the intrinsic electronic state of the metal. I will review the surface restructurings of metal model catalysts including different vicinal surfaces in different reactant gases. In addition, the in-situ studies of Pt(110) and Rh(110) during CO oxidation will be taken as two examples to illustrate the in-situ studies of surfaces of metal model catalysts under reaction conditions (in a gas phase of one reactant) and during catalysis (in a mixture of all reactants of a catalytic reaction).

3:00pm **SP+AS+BI+NS+SS-ThA3 Numerical Analysis of Amplitude Modulation Atomic Force Microscopy in Aqueous Salt Solutions**, *P. Karayaylalı*, ***Mehmet Z. Baykara***, Bilkent University, Turkey

We present a numerical analysis of amplitude modulation atomic force microscopy in aqueous salt solutions, by considering the interaction of the microscope tip with a model sample surface consisting of a hard substrate and soft biological material through Hertz and electrostatic double layer forces (P. Karayaylalı and M.Z. Baykara, *Applied Surface Science*, 2014, DOI: 10.1016/j.apsusc.2014.02.016). Despite the significant improvements reported in the literature concerning contact-mode atomic force microscopy measurements of biological material due to electrostatic interactions in aqueous solutions, our results reveal that only modest gains of ~15% in imaging contrast at high amplitude set-points are expected under typical experimental conditions for amplitude modulation atomic force microscopy, together with relatively unaffected sample indentation and maximum tip-sample interaction values.

3:20pm **SP+AS+BI+NS+SS-ThA4 Surface Potential Investigation of AlGaAs/GaAs Heterostructures by Kelvin Force Microscopy**, *S. Pouch*, ***Nicolas Chevalier***, *D. Mariolle, F. Triozon, Y.M. Niquet, T. Melin, Ł. Borowik*, CEA, LETI, MINATEC Campus, France

The Kelvin force microscopy (KFM) provides a spatially resolved measurement of the surface potential, which is related to the energetic band structure of a material. However, it depends strongly on the physical properties of the tip, e.g. width of the apex, the geometric shape and the stiffness of the cantilever as well as the surface sample state. The goal of this work is to investigate the surface potential measured by KFM on AlGaAs/GaAs heterostructures. For this study, we used a certified reference sample (BAM-L200), which is a cross section of GaAs and Al$_{0.7}$Ga$_{0.3}$As epitaxially grown layers with a decreasing thickness (600 to 2 nm) and a uniform silicon doping (5x10^{17} cm^{-3}). The resulting stripe patterns are commonly used for length calibration and testing of spatial resolution in imaging characterization tools (ToF-SIMS, SEM, XPEEM..) The surface potential measurement is performed under ultra-high vacuum with an Omicron system by using two acquisition modes: the amplitude modulation (AM-KFM), sensitive to the electrostatic force and the frequency modulation (FM-KFM), sensitive to its gradient. Three kinds of tips have been used for this study: platinum or gold nanoparticles coated silicon tips and super sharp silicon tips.

We will present the measurements obtained with these different tips for the narrowest layers (typ. < 40 nm). The surface potential mapping reveals a contrast around 300 meV between Al$_{0.7}$Ga$_{0.3}$As and GaAs layers. However, we observed that this contrast vanishes when layer thickness becomes thinner. This loss of contrast cannot be only explained by the resolution limit of the KFM technique. Indeed, we will discuss the effect of the band bending length scale at the AlGaAs/GaAs interface related to the dopant concentration. The contribution of band bending between the layers is evaluated by a self-consistent simulation of the electrostatic potential, accounting for the free carriers distribution inside the sample and for the surface and interface dipoles. We will show that the electric fields of the narrowest layers recover each other, resulting in the partial or total loss of the contrast between Al$_{0.7}$Ga$_{0.3}$As and GaAs layers. The simulation results will be compared to the experimental results in order to emphasize that the surface potential contrast is not only influenced by the resolution limit.

4:00pm **SP+AS+BI+NS+SS-ThA6 Probing the Quantum Nature of Hydrogen Bonds at Single Bond Limit in Interfacial Water**, ***Ying Jiang***, Peking University, China **INVITED**

Quantum behaviors of protons in terms of tunneling and zero-point motion have significant effects on water properties, structure, and dynamics even at room and at higher temperature. In spite of tremendous theoretical and experimental efforts, accurate and quantitative description of the quantum nuclear effects (QNEs) in water is still challenging, due to the difficulty of accessing the internal degrees of freedom of water molecules. Using a low-temperature scanning tunneling microscope (STM), we are able to resolve in real space the internal structure, that is, the O-H directionality, of individual water molecules adsorbed on a solid surface [1,2]. The key steps are decoupling electronically the water from the metal substrate by inserting an insulating NaCl layer and enhancing the molecular density of states of water around the Fermi level via tip-water coupling. These techniques allow us not only to visualize the concerted quantum tunneling of protons within the H-bonded network, but also to determine the impact of proton delocalization on the strength of hydrogen bonds by resonantly enhanced inelastic electron tunneling spectroscopy (IETS).

Key words: STM, IETS, water, QNEs, proton transfer, H-bonding strength

[1] J. Guo, X. Z. Meng, J. Chen, J. B. Peng, J. M. Sheng, X. Z. Li, L. M. Xu, J. R. Shi, E. G. Wang*, and Y. Jiang*, "Real-space imaging of interfacial water with submolecular resolution", Nature Materials 13, 184 (2014).

[2] J. Chen, J. Guo, X. Z. Meng, J. B. Peng, J. M. Sheng, L. M. Xu, Y. Jiang*, X. Z. Li*, E. G. Wang, "An unconventional bilayer ice structure on a NaCl(001) film", Nature Communications 5, 4056 (2014).

4:40pm **SP+AS+BI+NS+SS-ThA8 Resonant Enhanced Spectroscopy of Molecular Rotations with the STM and Field Effect Control of Molecular Dynamics**, ***Fabian Natterer***, *F. Patthey,* Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland*, Y. Zhao, J.E. Wyrick, J.A. Stroscio,* NIST*, H. Brune*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland

Inelastic electron tunneling spectroscopy (IETS) with the scanning tunneling microscope (STM) has vastly fueled the study of magnetic, electronic and vibrational properties of individual atoms and molecules due to its unmatched spatial and excellent energy resolution. Recently [1,2], rotational excitations could be characterized with IETS for the first time and yielded valuable insights into surface dynamics, bond lengths, and, notably about the nuclear spin state of homonuclear molecules. In particular, the two alike nuclei induce symmetry constraints in consequence of the Pauli principle and a certain alignment of nuclear spins requires a specific set of rotational levels J. We demonstrate rotational excitation spectroscopy (RES) with the STM for hydrogen, its isotopes, and mixtures thereof, physisorbed on metal supported graphene and hexagonal boron nitride, as well as on exfoliated graphene devices. We observe excitation energies that are equivalent with rotational transitions ($\Delta J = 2$) of molecules in the gas phase for hydrogen, hydrogen-deuteride, and deuterium, respectively. Notably, these values represent the nuclear spin isomers *para*-H_2 and *ortho*-D_2. For HD, an additional $J = 0 \rightarrow 1$ transition is discerned, which is allowed for heteronuclear diatomics. We discuss the excitation mechanism in the light of resonant enhanced tunneling [3,4], and illustrate how the dynamics of molecules could be controlled by applying an electric field using a back gating graphene device geometry [5].

[1] F. D. Natterer, F. Patthey, H. Brune, *Phys. Rev. Lett.***111**, 175303 (2013)

[2] Li *et al., Phys. Rev. Lett.***111**, 146102 (2013)

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[4] B. N. Persson, A. Baratoff, Phys. Rev. Lett. **59**, 339 (1987)

[5] J. Chae *et al.,Phys. Rev. Lett.***109**, 116802 (2012)

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Surface Science
Room: 309 - Session SS+AS+NS-ThA

Semiconductor Surfaces and Interfaces 1

Moderator: Ludwig Bartels, University of California - Riverside, Kurt Kolasinski, West Chester University

2:20pm **SS+AS+NS-ThA1 A Study of the InAs(001) Surface Electronic Structure**, ***Jacek Kolodziej***, *N. Tomaszewska, P. Ciochon*, Jagiellonian University, Poland

Angle-resolved photoelectron spectroscopy (ARPES) is used to study electronic bands at the n-type InAs(001) surfaces, having several different reconstructions. Indium-rich (8x2)/(4x2)and arsenic-rich c(2x8)/(2x4) surfaces as well as sulphur passivated (2x1) surface are prepared and investigated. Measured electronic bands are identified by analysis of their symmetries in the k-space.

In InAs crystal bulk the conduction band minimum (CBM) is located very close to the Fermi level (FL). Downward band bending, typical for the studied surfaces, causes formation of two dimensional electron gas, confined in a subsurface well, also known as the electron accumulation layer. This is indicated by characteristic quantized subband states visible in the ARPES spectra.

It is shown that the band bending magnitude and the quantization (of the accumulated electron energies associated with the coordinate normal to the surface) depend on the surface reconstruction as well as on the crystal doping. In most cases the electron accumulation bands are found at the Fermi level and close to the Γ_{1x1} symmetry point in the center of the surface Brillouin zone. The most clear picture is observed for the sulphur passivated (2x1) surface, where three distinct subbands with minima at E_1=-0,276eV, E_2=-0,096eV and E_3=-0,039eV with reference to Fermi level are found. Unexpectedly, for the indium rich surface, occupied conduction states are found also at Γ_{4x2} symmetry points indicating that, for this case, surface resonances mix with the electron accumulation states.

It is also shown that the observed surface bands are sensitive to surface treatment. Two surface preparation techniques have been used: cycles of ion beam annealing (IBA) and *ex situ* wet chemical treatment (WCT). Although low electron energy diffraction (LEED) indicates no increased disorder on the IBA surfaces they yield considerably worse electronic band images. This is most likely due to scattering of photoelectrons on the electrically active antisite defects.

We acknowledge financial support by Polish NCN (contract 2011/03/B/ST3/02070). The research was carried out with the equipment purchased thanks to European Regional Development Fund in the framework of the Polish Innovation Economy Operational Program (contract no. POIG.02.01.00-12-023/08).

2:40pm **SS+AS+NS-ThA2 Control of Point Defect Behavior in Metal Oxides via Surface Band Bending**, *M. Li, P. Gorai*, ***Edmund Seebauer***, University of Illinois at Urbana-Champaign

Point defects within metal oxide semiconductors such as ZnO affect the material's performance in applications for nanoelectronics, gas sensing, photonics and photocatalysis. Past work in this laboratory has shown that the presence of a nearby surface can influence the concentrations and spatial distributions of defects deep within the semiconductor – often in a controllable way. One mechanism for this influence involves band bending near the surface. The present work employs the optical modulation technique of photoreflectance to measure the magnitude V_S of band bending at polar c-axis ZnO surfaces, and demonstrates that V_S can be manipulated over a significant range (roughly 0.23-0.44 eV) through variations of both temperature and the ambient partial pressure of O_2. Separate modeling of charged oxygen interstitial motion within the ZnO indicates that the near-surface concentration of these defects scales quadratically with V_S, thereby pointing to a novel general approach by which bulk point defect concentrations can be controlled.

3:00pm **SS+AS+NS-ThA3 Evolution of Surface-Assisted Oxidation of GaAs by Gas-Phase N_2O, NO and O_2**, ***Xueqiang Zhang***, *S. Ptasinska*, University of Notre Dame

Interests in metal-insulator-semiconductor field effect transistors (MISFETs) have been re-ignited recently due to the approaching of the scaling limit of Si complementary metal-oxide-semiconductors (CMOS). The fate of the III-V semiconductors relies strongly on the availability of a suitable surface passivation technology for fabrication of high quality insulator/III-V semiconductor interface. Gallium oxides on GaAs represent one of contenders for suitable surface passivated oxide-based dielectrics that could produce device-quality electrical interfaces between the oxide and semiconductor. However, there has been a debate on possible GaAs oxidation mechanisms over years. A comparisonal study between O_2 and other reactive but heteronuclear molecules (such as NO and N_2O) near realistic conditions would provide new insights for a better understanding of the GaAs oxidation process.

A near-ambient pressure X-ray photoelectron spectroscopy (NAP XPS) study of interfacial chemistry between GaAs (100) and three oxidizing gases, N_2O, NO and O_2, are carried out in a wide range of pressures and temperatures. At room temperature, surface oxidation, involving the formation of both Ga_2O and Ga_2O_3 is observed with the extent of oxidation in the order of NO>O_2>N_2O at elevated pressures. At elevated temperatures, the extent of oxidation is in the order of O_2> NO >N_2O. Our experimental results show that the oxidation of GaAs (100) by N_2O and NO is primarily determined by the probability and nature of interactions at the gas/semiconductor interface, whereas the limiting factor in the case of O_2 is the energy requirement for O-O bond dissociation.

3:20pm **SS+AS+NS-ThA4 Morphology Dependence of Gas-Phase Molecule Interactions with GaAs Surfaces**, ***Sylwia Ptasinska***, *X.Q. Zhang*, University of Notre Dame

A great deal of progress has been made in understanding molecular interactions at the interface of two-dimensional GaAs systems under ultra-high vacuum (UHV) conditions. While research on understanding of such interactions with lower-dimensional GaAs-based structures, such as one-dimensional nanowires (NWs), has not been performed despite the potential importance of these structures for developing nano-electronic circuits. Moreover, surface characterization of GaAs under more realistic than the UHV studies, are critical in any attempt to correlate surface chemistry with device properties.

Nowadays, due to recent developments in the surface characterization techniques, and especially the development of Near Ambient Pressure X-ray Photoelectron Spectroscopy (NAP XPS) [1], we are able to track surface chemistry in-situ under elevated pressures and temperatures for different morphologies.

In our present study we used NAP XPS to investigate the interaction of a radically non-planar GaAs surface comprised of an ensemble of GaAs NWs with O_2 and H_2O molecules. In this study the evolution of O_2 and H_2O molecule dissociation on GaAs NWs is tracked under in-situ conditions as a function of temperature and gas pressure to establish whether these processes depend on surface morphology. In contrast to ideally flat GaAs single crystal surfaces that are previously studied [2], gas molecules experienced the enhanced dissociation on GaAs NW ensembles due to an increase in the surface area ratio and the presence of stepped edges, atom vacancies, and other defects on non-flat semiconductor surfaces [3].

[1] D. E. Starr, Z. Liu, M. Havecker, A. Knop-Gericke, and H. Bluhm, Investigation of solid/vapor interfaces using ambient pressure X-ray photoelectron spectroscopy, Chem. Soc. Rev. 42, 5833-5857 (2013)

[2] X. Zhang, S. Ptasinska, Dissociative Adsorption of Water on an H_2o/GaAs(100) Interface-in-Situ near Ambient Pressure XPS Studies, J. Phys. Chem. C 118, 4259-4266 (2014)

[3] X. Zhang, E. Lamere, X. Liu, J. K. Furdyna, S. Ptasinska, Morphology Dependence of Interfacial Oxidation States of Gallium Arsenide under near Ambient Conditions, Appl. Phys. Lett. DOI:10.1063/1.4874983 (2014)

4:00pm **SS+AS+NS-ThA6 STM Imaging of the Buried Interface Structures at Ultra-thin Ag Films/Si(111) Substrates**, *Y. Yoshiike, I. Kokubo, Y. Aoki, K. Nakatsuji*, ***Hiroyuki Hirayama***, Tokyo Institute of Technology, Japan

The Schottky barrier height (SBH) has been reported to change sensitively to the variety of reconstructions at the Si substrates before depositing metal films in such systems as Pb/Si(111) and Ag/Si(111). Meanwhile, metal and Si do not mix, and the interfaces between the metals films and Si substrates are atomically abrupt in these systems. Thus, reconstructions at the Si(111) substrate are regarded to be preserved at buried interfaces under metal films, and have an influence on the SBH. In this respect, direct characterization of the buried interface structures in real space is required.

Scanning tunneling microscopy (STM) is a potentially promising method to achieve this, although it is conventionally considered to be useful only for exposed surfaces. Substantially, two different patterns, which were regarded to reflect the periodicity of the lattice at the buried interfaces, were observed on ultra-thin Pb films on the Si(111) substrates. However, the relation to the buried interface structures and the reason for the visualization were still not elucidated. With regard to these points, it is of significant interest to examine whether a different reconstruction on the Si(111) substrate could cause various periodic patterns in abrupt interface systems other than the Pb/Si(111). It is also of interest to investigate the origin of the new periodic pattern. From this perspective, we investigated the STM images of ultra-thin Ag films on Si(111)√3×√3-B and Si(111)7x7 substrates in this study.

As results, ripples were observed at the surface of ultra-thin Ag films on a Si(111)√3×√3-B substrate system in STM and dI/dV images. The ripples were faint, independent of the bias voltage, and had the 3×3 periodicity. These indicate that the ripples were geometric corrugations formed at the Ag film surface, which were induced by the commensuration of the Ag(111)1×1 and Si(111)√3×√3-B lattices at the buried interface. In the meantime, a different ripples were observed at the surface of ultra-thin Ag films on a Si(111)7x7 substrate. The ripples were less periodic, but the Fast Fourier Transform of the images revealed that they had the 7x7 periodicity. In contrast to the Pb/Si(111)7x7 system, the ripples were independent of the bias voltage. Thus, the 7x7 ripple was also regarded to reflect the interface commensuration-induced geometric corrugations at the Ag film surfaces. More detailed results and Synchrotron radiated X-ray diffraction data of these buried interfaces will be shown and discussed in the presentation.

4:20pm **SS+AS+NS-ThA7 Ge on Si Epitaxy: Formation of 3D Ge Islands on Si(100)-2x1 by Annealing of Ge Wetting Layers**, ***Gopalakrishnan Ramalingam***, *P. Reinke*, University of Virginia

The epitaxial growth of Ge on Si(100)-(2x1) proceeds by Stranski-Krastanow (SK) mode where the formation of a wetting layer (WL) is followed by the emergence of quantum dots (QD). New growth modes have been reported recently which can lead to highly anisotropic Ge-wires and are achieved by annealing of the WL prior to the onset of QDs. The goal of the current work is to understand the atomistic processes involved in the transformation of the WL during annealing. We have investigated the WL structure during post-growth annealing at 400 to 600 C and report the transformation of epitaxial two dimensional Ge wetting layers into three dimensional islands, referred to here as pre-quantum dots (p-QDs). The p-QDs include hillocks with a stacked, wedding-cake type structure which show a progression to partial {105} faceting in case of thicker Ge WLs and longer anneal times. At low WL thickness (1-1.5 ML), the p-QDs have a stacked structure while thicker WLs (2-3.5 ML) lead to partial {105} faceted structures. All p-QDs, irrespective of the faceting or size, are characterized by an amorphous mound at the apex; this is strictly limited to p-QDs and not observed for regular QDs. The transition from the WL to p-QDs depends sensitively on the WL thickness (for a given annealing temperature): a six-fold increase in the island number density and a similar decrease in average island volume are observed when the initial WL thickness was increased from 1.2 to 3.5 ML. A small but notable increase in the island number density is observed when samples are annealed for longer durations (after the initial anneal to form the p-QDs) confirming that Ostwald ripening is not a dominant process in this system. Our observations will be integrated with a simulation of the growth process which will inform on the relevant mass transport and the role of strain on the WL transformation to p-QDs.

4:40pm **SS+AS+NS-ThA8 In Search of Nanopatterns: STM Provides Mechanistic Insights into Silicon Functionalization**, ***Erik Skibinski***, Cornell University, *W.J.I. DeBenedetti, Y.J. Chabal,* University of Texas at Dallas, *M.A. Hines*, Cornell University

Functionalization reactions leave characteristic patterns on surfaces that can be read by STM, providing insight into reaction mechanisms. The functionalization of silicon surfaces with organic monolayers has attracted interest for applications ranging from chemical and biological sensing to renewable energy. A wide variety of surface functionalization reactions have been developed based on dehydration reactions that target surface -OH groups on oxidized silicon. Uniform functionalization therefore requires a uniform, high density of surface –OH groups. Hydroxylating silicon surfaces without concomitant oxidation of the substrate was long thought impossible; however, a novel three-step strategy was recently reported.[1] A hydrogen-terminated silicon surface is first methoxylated in methanol, and then the Si–OCH$_3$ sites are converted first to Si–F then to Si-OH by successive immersion in hydrofluoric acid and water. Original spectroscopic evidence suggested the creation of nanopatterned surface, in which every other site on the surface is functionalized. New STM and spectroscopic data show selective reaction at step edges and an unexpected functionalization pattern. The mechanistic implications of this pattern will be discussed.

[1] D. J. Michalak, S. R. Amy, D. Aureau, M. Dai, A. Estève, and Y. J. Chabal, *Nat. Materials* **9,** 266 (2010).

5:00pm **SS+AS+NS-ThA9 Benzene and Chlorobenzene Dissociation Pathways Involving Singlet-Triplet Crossing on the Si(100) Surface Modeled Using Small Clusters**, ***Nicholas Materer****, E. Butson,* Oklahoma State University*, Q. Zhu*, University of Pittsburgh

The dimer rows in the Si(100) surface have di-radical character, which can be configured as a singlet or triplet. At the minimum energy crossing point of the singlet to triplet crossing for a single Si-dimer cluster, the spin-orbit coupling (SOC) coefficient was determined to be approximately 25 cm^{-1}. Using this SOC, the Landau-Zener spin-crossing probability at room temperature was computed to be approximately 0.5%. Similar computational methods were used to investigate possible adsorption and dissociation processes for benzene and chlorobenzene. The 1,2 product (a tilted configuration) for benzene adsorption was proposed to undergo C-H bond cleavage to form lower-energy products. However, this process requires a spin-crossing of the initial 1,2 bond product, followed by a transition state with large activation barriers. Chlorobenzene can absorb on the SI(100) by breaking one double bond on the phenyl ring and forming two new carbon-silicon bonds with the dimer cluster. Again, for dissociation to occur, the system must undergo a spin crossing process from the singlet to the triplet state. After this spin crossing event, the carbon-chlorine bond is cleaved and a new silicon-chloride bond is formed. The final product is a dissociation product with chlorine and a phenyl ring attached directly to the (100) surface of silicon. Both cases illustrate that spin crossing could be more common than realized in the adsorption and dissociation of organic molecules on Si(100).

5:20pm **SS+AS+NS-ThA10 Adsorption of Organic Triols on Ge(100)-2x1 Surface**, ***Tania Sandoval****, S.F. Bent*, Stanford University

Organic functionalization of semiconductor surfaces can provide tunable control of interfacial properties in organic-inorganic hybrid devices. The key step toward applications in this area is to understand the selectivity in the reactions of organic molecules on these surfaces.

In this work, adsorption of 1,3,5-benzenetriol and 2-hydroxymethyl-1,3-propanediol on Ge(100)-2x1 surface was studied. Both molecules have three hydroxyl groups available for reaction with the Ge surface. While the reactions of these molecules with the surface may be similar, differences in reactivity can be expected due to their different backbone structures. The aim of this study is to investigate whether a difference in reactivity exists and how the reaction with the surface is affected by the structure of the molecules.

Energy diagrams for both molecules were calculated by density functional theory. In both cases, proton transfer reactions from two or three hydroxyl groups to the Ge dimer atoms are suggested as thermodynamically favored pathways. However, the reaction through 3 OH groups in 2-hydroxymethyl-1,3-propanediol is more than 15 kcal/mol more stable than the same reaction in 1,3,5-benzenetriol. This difference can be associated with strain of the aromatic ring.

Infrared spectroscopy (IR) and X-ray photoelectron spectroscopy (XPS) were performed to investigate the adsorption products. IR results show the presence of a ν(Ge-H) mode for both molecules, suggesting the proton transfer reaction as the main pathway. XPS spectra of each molecule both chemisorbed and physisorbed on the surface were obtained. The differences between these two spectra can be used to indicate the reaction products. For both molecules, no change in the C(1s) spectra is observed, suggesting that carbon does not form a bond directly with Ge. On the other hand, clear differences between the chemisorbed and physisorbed O(1s) spectra are observed for both molecules. A second peak with a lower binding energy only in the chemisorbed spectra, assigned to a Ge-O bond confirms that both molecules react with the Ge surface through O-H dissociation. The ratio between O(1s) peaks indicates that about 80% of the total hydroxyl groups are involved in reaction with Ge, suggesting that a significant fraction of the adsorbates react with the surface through all 3 of their hydroxyl groups.

In conclusion, both 1,3,5-benzenetriol and 2-hydroxymethyl-1,3-propanediol react with the Ge(100)-2x1 surface through O-H dissociative adsorption. Little difference in reactivity was observed between these triols, suggesting that other factors besides backbone structure are governing the reactivity in these systems.

5:40pm **SS+AS+NS-ThA11 The Chemistry of Adsorbed Water on Semiconductor Surfaces for Aqueous Photoelectrochemistry**, ***Coleman Kronawitter****, B. Koel*, Princeton University

The surface chemistry of water molecules adsorbed on single crystals, model structures relevant to photoelectrode-water interfaces in solar photoelectrochemical systems, is discussed. In heterogeneous processes relevant to photoelectrochemistry, the interaction of water with semiconductor and metal oxide surfaces is often a critical event whose character influences subsequent chemical pathways that ultimately dictate the reactions' efficiencies and selectivities. A surface science approach is used to characterize adsorbed water molecules on copper oxide and III-V semiconductor surfaces known to actively facilitate solar energy conversion in photoelectrochemical fuel synthesis devices. In this approach, ultrahigh vacuum conditions are used to facilitate the fabrication of highly characterizable adsorbate systems, and the use of single crystal substrates permits analysis of surface chemistry independent of sample grain boundaries and morphology. An understanding of the surface chemistry of adsorbed water is developed through core-level spectroscopies and scanning probe microscopy.

Scanning Probe Microscopy Focus Topic
Room: Hall D - Session SP+AS+EM+NS+SS-ThP

Scanning Probe Microscopy Poster Session

SP+AS+EM+NS+SS-ThP2 Fabrication of Single-Walled Carbon Nanotube Probe and Processing of Single Nanometer Scale Pit with High-Aspect-Ratio of Highly Oriented Pyrolytic Graphite Using by STM, ***Syun Ohsumimoto***, *A. Matsumuro*, Aichi Institute of Technology, Japan

Our unique fabrication methods of high-aspect-ratio nanometer scale three-dimensional structures of pits, lines and convex parts using a multi-wall carbon nanotube (MWNT) with diameter of about 50 nm as a STM probe have been developed successfully. It turn out that this method has been applicable to surfaces of various conducting materials, such as noble metal thin films, low-resistivity single crystalline silicon wafer and highly oriented pyrolytic graphite (HOPG). We also have clarified that the physical origin of this nanometer-scale pit processing using STM must be the field evaporation mechanism by the results of TEM *in-situ* observations during fabrication process. In order to realize further ultra-precise three dimensional structures with high aspect ratio, it is surely required that a innovative ultimate ultra-precision processing technology needs fabrication size below several nm, i.e. single nanometer scale.

This study paid great attention to realize the ultimate processing of single nanometer scale structures using a single-wall carbon nanotube (SWNT) probe as our original STM processing. The most important problem was to overcome to much difficulty in synthesis of SWNT probes with high probability. Then, the application of mixed dispersion liquid containing both MWNTs and SWNTs could be devised at the process of producing SWNT probes. In this process, it was clarified that the SWNT easily attached to the point of the MWNT, which was easily adhered to the apex of the conventional tungsten needle through the pulling method that we developed originally. The success rate for synthesis of the SWNT probes with diameters of about 2 nm and 10 nm were drastically increased up to about 10 % and 14 %, respectively. As compared with the case where the dispersion liquid of only SWNT is used, success fabrication rate has been nearly equal to 0 %. Single nanometer scale pits were actually fabricated on HOPG in atmosphere and room temperature condition. The SWNT probe with diameter of about 2 nm under the conditions of a bias voltage of 5 V, tunnel current of 1 nA and fabrication time of 60 s could realize a single nanometer scale pit with the diameter of 9 nm and the depth of 13 nm. The aspect ratio with SWNT probes increased up to about 5 times in the case of MWNT probes. These demonstrate that these STM fabrications by using SWNT probes with several diameters must give a remarkable effect in fabricating three-dimensional high-aspect-ratio structures with single nanometer-scale.

SP+AS+EM+NS+SS-ThP3 Probing the Electronic Structure of the Layered Electride Ca_2N, ***Jeonghoon Ha***, NIST/Maryland Nano Center, University of Maryland, *H. Baek,* NIST & Seoul National University, Republic of Korea, *D. Zhang,* NIST/Maryland Nano Center, University of Maryland, *Y. Kim, S. Kim, Y.J. Song,* Sungkyunkwan University, Republic of Korea, *Y. Kuk,* Seoul National University, Republic of Korea, *J.A. Stroscio*, NIST

Electrides are electronic materials in which excessive electrons are confined into cavities defined by the crystal structure. These excessive electrons take the place of negatively charged ions in an ionic crystal. The geometry of the cavities confining these anionic electrons determines the electronic properties of the material and provides a platform to study various interaction physics [1]. A previous study reported the inorganic electride Ca_2N to have a layered structure with anionic electrons confined to 2-dimensional cavities between the cationic crystal layers [2]. In this previous study, transport measurements showed high electron mobility and long mean scattering time, and magneto-resistance measurements confirmed diffusive 2-dimensional transport in the electron layers.

In the present work, we use an ultra-low temperature scanning tunneling microscope to investigate the local electronic structure of a cleaved surface of a Ca_2N single crystal. An energy gap was observed in the tunneling spectrum with a gap size of 0.4 meV. The spectra contain multiple coherence-like peaks which are equally spaced in energy, suggestive of possible multi-band superconductivity or quantum confinement in the electron layers. Temperature-dependent tunneling spectroscopy measurements show a gradual suppression of the energy gap up to 2.5 K. An interesting observation is that the gap structure and the peak features do not get suppressed in the presence of a perpendicular magnetic field up to 14.5 T, suggesting if the crystal is in a superconducting state, then the critical field is extremely large compared to the transition temperature. These observations and further discussion of possible unconventional superconductivity will be discussed in this presentation.

[1] J. Dye, Science **301**, 607 (2003)

[2] K. Lee *et al*, Nature **494**, 336 (2013)

SP+AS+EM+NS+SS-ThP5 Improving the Accuracy of Atomic Force Microscopy in Nanometrology for Linewidth Measurements, ***James Su,*** *N.N. Chu, M.H. Shiao, C.N. Hsiao*, Instrument Technology Research Center, National Applied Research Laboratories, Taiwan, Republic of China

Atomic force microscopy (AFM) has an important role in dimensional metrology especially in the nanoscale. The morphology image processed by the AFM is the interaction between the tip and the sample surface. The result of the interaction may cause broadening of peaks and shrinking of valleys in the scanning process caused by tip effects. It would be impossible to differentiate the portion due to the tip and the portion due to the sample surface without determining the tip geometry which is a key role in AFM-image quality. As a case study, AFM measurements of nanowires (NW), carbon nanotubes (CNT) and nano-honeycombs fabricated by nanosphere lithography (NSL) technology are examined. Line width measurement results may expand up to 39.5% by adopting a conventional pyramid-shaped probe and 17.5% by using a conical-shaped one as the dimensions of the scanned features approaches to the order of magnitude of the tip apex. The uncertainty of measurement would expand if tip wear occurs during image scan. Calculation for surface reconstruction has been developed to extract the part related to the tip from the SPM image. The SPM used for these measurements is equipped with a highly accurate scanning system, which employs closed-loop capacitive feedback control to ensure outstanding linearity and position accuracy. To identify the geometry of the tip, a silicon tip characterization grating was imaged between the measurements. Deconvolution process were carried out for topography image corrections, and the results were further compared with the ones measured from the scanning electron microscope (SEM). This process is essential to derive accurate measurement results in the nanoscale region.

SP+AS+EM+NS+SS-ThP8 The Effect of Electrochemical Potential on Single Molecule Conductance, ***Esteban Sanchez***, *R. Aguilar,* BUAP, Mexico, *S. Afsari,* Temple University, *Z. Li,* Ball State University, *E. Borguet*, Temple University

Porphyrins have been widely studied for their electrochemical properties to understand charge transfer. The related property of charge transport can be accessed by single molecule conductance (SMC) measurements. The most common SMC studies involve transport between different anchor groups at transversal positions in the molecule [1]. Few investigations have been made using porphyrins lying flat on the substrate in electrochemical environment [2]. Recent studies have shown that the templating effect of self-assembly can be exploited to orient molecules in metal-molecule-metal junctions, so that transport perpendicular to the molecular plane can also be easily accessed [3].

This goal research is to use self assembly, verified by scanning tunneling microscopy (STM), to measure charge transport in single porphyrins adsorbed flat on the Au (111) surface. 5,10,15,20-Tetra(4-pyridyl)porphyrin (TPyP) is a good candidate for this research because it has been demonstrated that this porphyrin has a strong interaction with, and can form ordered layers on, Au (111) in electrochemical environment [4]. This control of the orientation of the porphyrin by electrochemical potential enables us to make SMC measurements perpendicular to the molecular plane.

[1] Zhihai Li, Manuel Smeu, Mark A. Ratner, and Eric Borguet, Effect of Anchoring Groups on Single Molecule Charge Transport through Porphyrins, J. Phys. Chem. C, **117**, 14890−14898 (2013).

[2] Quirina Ferreira, Ana M. Braganca, Luís Alcacer, and Jorge Morgado, Conductance of Well-Defined Porphyrin Self-Assembled Molecular Wires up to 14 nm in Length, J. Phys. Chem. C, **118**, 7229−7234 (2014)

[3] Sepideh Afsari, Zhihai Li, and Eric Borguet, Orientation-Controlled Single-Molecule Junctions, Angew. Chem. Int. Ed. **53**, 9771 –9774 (2014).

[4] Tao Ye, Yufan He, and Eric Borguet, Adsorption and Electrochemical Activity: An In Situ Electrochemical Scanning Tunneling Microscopy Study of Electrode Reactions and Potential-Induced Adsorption of Porphyrins, J. Phys. Chem. B, 110, 6141-6147 (2006).

Atom Probe Tomography Focus Topic
Room: 301 - Session AP+AS+NS+SS-FrM

Correlative Surface and Interface Analysis with APT
Moderator: Arun Devaraj, Pacific Northwest National Laboratory

8:20am **AP+AS+NS+SS-FrM1 Correlative Transmission Electron Microscopy and Atom Probe Tomography of Interfaces in CdTe**, ***David Diercks***, *J.J. Li, C.A. Wolden, B.P. Gorman*, Colorado School of Mines **INVITED**

CdTe solar cells are a promising thin film technology, yet the highest reported efficiencies [1] remain well below the theoretical efficiency for such materials. For polycrystalline CdTe, interface contacts and grain boundaries along with impurities likely account for the majority of this underperformance.

Atomic scale analysis is an important feedback mechanism to relate the structure to both the device performance and the processing conditions. Through this, the atomic scale factors which improve or limit the performance can be ascertained. This then enables the development of materials and processing methods which best eliminate or mitigate the detrimental effects.

With these goals, atom probe tomography (APT) in conjunction with transmission electron microscopy (TEM) was used to study the contact interfaces and grain boundaries in CdTe devices. With the combination of time-of-flight mass spectrometry and point projection microscopy by controlled field evaporation, APT has the ability to obtain tens of ppm composition sensitivity along with near atomic-level spatial resolution. TEM provides crystallographic information along with other correlative information for guiding the reconstruction of the APT data.

It is demonstrated that the compositions measured for CdTe by APT are sensitive to the analysis conditions. Therefore, the APT analysis conditions for obtaining accurate measurements of the specimen stoichiometry were first ascertained. Following that, TEM and APT analyses of thin film devices consisting of a fluorine-doped tin oxide coated glass substrate subsequently coated with CdS, CdTe, Cu-doped ZnTe, and Au were performed. Using optimized values, APT analyses on the absorber layers and contact interfaces after different deposition and processing conditions were performed. These show significant changes in copper and sodium distributions as a result of the thermal processing.

[1] M. A. Green, K. Emery, Y. Hishikawa, W. Warta, and E. D. Dunlop, "Solar cell efficiency tables (version 42)," *Progress in Photovoltaics,* vol. 21, pp. 827-837, Aug 2013.

9:00am **AP+AS+NS+SS-FrM3 Atom Probe Compositional Analysis of Nanoscale Precipitates in Nb-Ti Micro-alloyed Steels**, ***Monica Kapoor***, *G.B. Thompson,* University of Alabama, *R.M. O'Malley*, Nucor Steel

Composition of complex carbide and carbo-nitride precipitates in Ti-Nb micro-alloyed 80-ksi (0.06 wt. % Nb; 0.06 wt. % Ti) and 100-ksi (0.03 wt. % Nb; 0.12 wt. % Ti) steels was studied using atom probe tomography. Fine (~2 nm) and coarse (~8 nm) NbTiC precipitates were identified in the 100 ksi steel with the Fe content decreasing with increasing precipitate size. Both steels had coarse NbTiCN precipitates (~ 80 nm) having ~7 at. % and ~30 at. % Nb in the precipitates for the 100 ksi and 80 ksi steels respectively. Star-shaped TiC precipitates and parallel rows of interphase NbTiC clusters on and near grain boundaries were also identified in the 100 ksi steel. In the 80 ksi steels, uniformly distributed disk-shaped and spherical NbTiC clusters were observed along dislocations. The composition and phase stability of these precipitates are discussed in terms of Thermo-Calc solution thermodynamic modeling.

9:20am **AP+AS+NS+SS-FrM4 Nanoscale Imaging of Li and B in Glass Samples, a Comparison of ToF-SIMS, NanoSIMS, and APT**, ***Zihua Zhu***, *Z.Y. Wang, J. Liu, J. Crum, J.V. Ryan, D.K. Schreiber, J.J. Neeway*, Pacific Northwest National Laboratory

A widely used method to immobilize nuclear wastes is fusing them into glasses. These proposed glass waste forms are multicomponent complex material with the common components of Li and B compounds. It is difficult for commonly-used surface analysis tools (e.g., X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy, scanning electron microscope/energy dispersive spectroscopy (SEM/EDX), and transmission electron microscope/energy dispersive spectroscopy (TEM/EDX)) to image the distributions of ultra-light elements like Li and B with sub-micron lateral resolutions. Time-of-flight secondary ion mass spectrometry (ToF-SIMS), NanoSIMS, and atom probe topography (APT) were used to image Li and B distributions in several representative glass samples. ToF-SIMS can provide ~100 nm lateral resolutions if using Li^+ and BO_2^- images. However, both positive ion mode and negative ion mode are needed because neither B signals in positive ion mode nor Li signals in negative ion mode can provide adequate intensity to form qualified images. NanoSIMS can provide ~100 nm lateral resolutions if using Li^- and BO_2^- images, while the lateral resolution of positive ion mode of NanoSIMS is poor (~400 nm). APT can provide ~2 nm lateral resolution for Li^+ and B^+ in a 3-D mode and quantification of APT is better than that of SIMS. While APT can provide much better ultimate lateral resolution than ToF-SIMS and NanoSIMS, it has three drawbacks: limited field-of-view, time-consuming sample preparation, and frequent/unpredicted sample damage during measurement. As a comparison, field-of-view of SIMS is flexible, sample preparation is simple, and little unpredicted sample damage occurs during SIMS measurement. Therefore, SIMS and APT can be regarded as complimentary techniques in nanoscale imaging of Li and B in glass samples.

9:40am **AP+AS+NS+SS-FrM5 Application of (S)TEM and Related Techniques to Atom Probe Specimens**, ***William Lefebvre***, *D. Hernandez-Maldonado, F. Cuvilly, F. Moyon*, University of Rouen, France **INVITED**

The geometry of atom probe tomography (APT) specimens strongly differs from standard scanning transmission electron microscopy (STEM) foils. Whereas the later are rather flat and thin, APT tips display a curved surface and a significantly larger thickness. As far as a correlative approach aims at analysing the same specimen by STEM and APT, it is mandatory to explore the limits and advantages imposed by the particular geometry of APT specimens to STEM.

High angle annular dark field (HAADF) in STEM provides a contrast related to atomic number and to the amount of atoms in a column. A complete analysis of a high resolution HAADF STEM image requires the identification of projected column positions, the calculation of integrated HAADF intensity for each column and, eventually, the estimation of a "background level" generated by the amorphous carbon or oxide layer present on the specimen surface. Then, by of a statistical analysis [1], the possibility of atomic counting in an APT specimen can be explored. For this purpose, we propose an image processing method which provides a complete analysis of HAADF STEM images, that was applied here to APT specimens. In order to estimate the advantages and limitations of the method for such a particular specimen geometry, simulations have been applied and confronted to experimental results. Illustrations will be given for specimens before and after field evaporation in APT.

[1] S. Van Aert et al. Phys. Rev. B 87 (2013) 064107

10:40am **AP+AS+NS+SS-FrM8 APT Analysis of Biological Materials**, ***Daniel Perea***, *J. Liu, J.A. Bartrand, N.D. Browning, J.E. Evans*, Pacific Northwest National Laboratory **INVITED**

Biointerfaces play an essential role for the function of many biological materials and organisms. The behaviors of complex macromolecular systems at materials interfaces are important in the fields of biology, environmental biology, biotechnology, and medicine. An understanding of the chemical processes and physics, and ultimate the ability to engineer biomaterials and microorganisms with specific properties and functions, is aided by an atomic level understanding of the composition and morphology of biointerfaces. However, a great challenge exists to map the atomic level composition and morphology of biointerfaces using APT, precluding a complete understanding of the structure properties relationship. At the Environmental Molecular Sciences Laboratory (EMSL), the application of APT is being developed in combination with other microscopy and spectroscopic techniques to study interfaces in biologic materials. We are developing methodologies and analyses that are allowing us to probe the ultimate limits of what APT analysis can confidently provide despite the complex thermally-assisted field evaporation behavior of soft materials. Advanced sample preparation techniques will also be discussed that further advance the application of APT into field of biology.

Applied Surface Science
Room: 316 - Session AS+MC+SS-FrM

Practical Surface Analysis II
Moderator: Steven Pachuta, 3M Company

8:20am **AS+MC+SS-FrM1 Vector Potential Photoelectron Microscopy**, ***Raymond Browning***, R. Browning Consultants

Vector potential photoelectron microscopy (VPPEM) is a new class of synchrotron based analytic spectromicroscopy using NEXAFS and XPS spectroscopy. To optimize the spatial resolution VPPEM images very low energy photoelectrons which poses both challenges and opportunities. At low energies the NEXAFS signals have an information depth that is similar to that from total yield absorption (TAY) measurements, while the XPS signals have a variable information depth from the universal curve at low energies. VPPEM has a very high depth of focus, and immunity to many imaging artifacts such as surface charging, and magnetic state. This makes VPPEM suitable for analyzing real world samples, and we present some results from the prototype instrument at NSLS.

8:40am **AS+MC+SS-FrM2 Hydrogen and Chemical Quantification of an Organic Coating**, ***Paul Mack***, Thermo Fisher Scientific, UK

Zinc-coated steel substrates often have an additional organic coating applied, protecting the steel surface or altering its appearance for decorative reasons. X-ray Photoelectron Spectroscopy (XPS) is an analysis technique which provides chemical bonding information from the top few nanometres of a surface down to many microns in depth. It is the ideal technique, for example, for identifying the carbon functional groups in these organic coatings. XPS cannot detect hydrogen, however, but the complementary technique of Reflection Electron Energy Loss Spectroscopy (REELS) is able to both detect and quantify hydrogen. REELS can also be used to discern between aliphatic and aromatic carbon in the organic coatings.

There is also a requirement for compositional profiling of these coatings, combining the excellent depth resolution and chemical specificity of XPS with some kind of ion beam sputtering. Traditional methods such as argon monomer ion profiling can result in a high degree of chemical modification during the acquisition of depth profiles for organic materials. Numerous studies over recent years, however, has shown that argon cluster beams may be used for depth profiling while preserving chemical information during analysis of organic materials.

This talk will present data from cluster profiling studies of an organic coating on steel. The data will be compared with an alternative method of profiling the coating, i.e. ultra low angle microtomy. A complete elemental compositional profile of the coating, including hydrogen, will be presented.

9:00am **AS+MC+SS-FrM3 Mechanical Strain Induced Tunable Reflective and Conducting Silver Nanorods Embedded PDMS Film**, ***Pratibha Goel****, *J.P. Singh*, Indian Institute of Technology, India

The formation of metallic films on both inorganic and organic polymeric substrate continues to be of substantial interest because of various applications.[1,2] Polymeric supports offer the obvious advantages in weight, flexibility, elasticity, and fragile relative to inorganic support such as glasses, ceramics, or native metal. Silver is a metal of choice as a reflecting material because of its high reflection coefficient (0.93). Silver also has the highest electrical conductivity of all metals at 6.3×10^7 $(\Omega m)^{-1}$. However, there are disadvantages of using silver as the reflecting metal. Firstly, silver is a relatively soft metal so that the face of a mirror needs to be carefully protected from mechanical abrasion. Secondly, silver tends to tarnish which diminishes its reflectivity. (Ambient sulfur-containing compounds are a particular problem.) Thirdly, and perhaps the most important, silver(0), as a more passive metal, does not interact strongly with organic functionalities, which means that adhesion of a silver layer on a polymer surface can be a substantial problem.

In this study we present a straightforward two step fabrication of highly adherent, reflective and surface conductive flexible films. First, the Ag nanorods were deposited on the Si (001) substrates by thermal evaporation of silver powder using oblique angle deposition (OAD).[3] Then the thermal curing of the PDMS on the Ag nanorods grown Si wafer leads to the copolymerization yielding a flexible, reflective and conductive silver surface approaching that of the native film. The Fig. 1 shows schematically the route followed for the fabrication of the sample. As prepared sample appear to be highly reflecting and conducting with the reflectance (R) of 64.17 % at 530 nm and sheet resistance (R_s) of 24.03 Ω/sq. Elongation of the sample up to 30% of its original length results into decrease in the reflectance and increase in R_s. Fig. 2 shows the tunability of the R at 531 nm and R_s with respect to the strain applied. Adhesion between the silver nanorods and the polymeric PDMS film was outstanding. No adhesive tapes removed any silver from the surface. Our sample may find potential applications in multifunctional devices where tunability of reflectance and conductivity is desirable through flexibility.

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9:40am **AS+MC+SS-FrM5 Surface Analysis of Electronic Materials**, *R.L. Opila*, ***Kevin Jones***, *J. Church*, University of Delaware, *R. Gupta, V. Pallem, B. Lefevre*, Air Liquide, *X. Lin*, University of Delaware

Surface analysts at the University of Delaware have used a variety of surface analytical techniques to analyze films for electronic materials applications. These films were deposited by a variety of technique including plasma enhanced chemical vapor deposition, molecular organic chemical vapor deposition and atomic layer deposition using precursors synthesized at Air Liquide. Methods of analysis include x-ray photoelectron spectroscopy, scanning Auger electron spectroscopy, time-of-flight secondary ion spectrometry, nano-indentation and synchrotron-based hard x-ray analysis. The advantages of each technique for particular analyses will be discussed.

10:40am **AS+MC+SS-FrM8 Lewis Base Sites on the Nitrogen-Doped Graphite Surfaces Probed by CO_2 Adsorption**, ***Takahiro Kondo***, *R. Shibuya, S. Morohoshi, D. Guo, J. Nakamura*, University of Tsukuba, Japan

Carbon materials have been reported to exhibit unique adsorption property and catalytic activity when they have received specific treatments such as nitrogen doping. For example nitrogen-doped graphene has been reported to show the superior catalytic activity for the oxygen reduction reaction (ORR) in fuel cell [1]. To understand the origin of such specific properties at the atomic scale, we are now trying to examine the relationship among the localized electronic states of the carbon atoms, the adsorption property of the molecule, and the catalytic activity towards ORR by using model catalyst of graphite with surface science techniques. Previously, we have reported based on the scanning tunneling spectroscopy (STS) that the carbon atoms around a pyridinic-nitrogen (N having two N-C bonds) in a highly oriented pyrolytic graphite (HOPG) have occupied localized states near the Fermi level [2]. We consider that such carbon atoms may act as Lewis base sites [2] and may relate to the ORR activity. In this work, we have examined this hypothesis by observing the carbon dioxide adsorption property with temperature programmed desorption (TPD), ORR catalytic activity measurement, and X-ray photoelectron spectroscopy (XPS).

To prepare the pyridinic-nitrogen-doped graphite (pN-HOPG) as the model catalyst, we have firstly cleaved the HOPG at atmosphere and then bombarded it by the nitrogen ion through Ni patterned mask to make edges with N-termination. After the bombardment, the sample was put into HNO_3 solution for 72 hours to remove Ni impurity. The sample was annealed at 900 K for 2 hours in ultrahigh vacuum. XPS spectrum shows that the nitrogen in the prepared sample consists of over 60 % pyridinic-nitrogen, suggesting that nitrogen atoms are dominantly doped at the edges.

In TPD measurements, CO_2 desorption peak was observed at around 370 K from pN-HOPG after the 1000 L CO_2 exposure at 300 K, while no CO_2 desorption peak was observed from clean HOPG. These results indicate that Lewis base sites are formed on pN-HOPG. The same CO_2-TPD results were reproducibly observed by sequential 4 time measurements. This means Lewis base sites on pN-HOPG does not change by the CO_2 adsorption and desorption. Details of CO_2 adsorption properties on pN-HOPG, the relationship with ORR activity and the influence of nitrogen configuration on the carbon atoms in pN-HOPG will be discussed.

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11:00am **AS+MC+SS-FrM9 Towards Spin-FETs: Growth and Characterization of Magnetoelectric Chromium Oxide Films on Graphene**, ***Sean Stuart***, *E. Sachet, J.-P. Maria, J.E. Rowe, D.B. Dougherty,* North Carolina State University, *M. Ulrich*, Army Research Office

Graphene has brought spintronic devices that depend on the ability to transport spin much

closer to realization. Graphene's high carrier mobility and low spin-orbit scattering allow for efficient

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*** ASSD Student Award Finalist**

spin transport, which has been demonstrated by several publications over useful length scales [1,2].

Further progress toward more sophisticated spintronic devices requires controllable manipulation of

spin polarized charge carriers. A graphene Spin-Field Effect Transistor has been proposed by

Semenov et al [3] that manipulates the spin of charge carriers in a graphene channel by an exchange

interaction with a hypothetical ferromagnetic dielectric. As an alternative that also adds functionality,

we have identified Cr2O3 as a material whose magnetoelectric properties would enable voltage

controlled switching of the exchange interaction. The Magnetoelectric properties of Cr2O3 have been

extensively studied [4], including recent reports of a robust electrically switched magnetic surface

state [5,6].

We used pulsed laser deposition to grow thin Cr2O3 films directly on HOPG. AFM shows a

smooth Cr2O3 film with the hopg topography preserved. X-Ray Diffraction shows that the film has a

(0001) texture for films grown at 300 - 650ºC, which is the strongest orientation of the

magnetoelectric effect. The magnetic polarization of the film can be aligned by magnetoelectric

annealing and locally switched with conducting AFM, the effects of both are observed by magnetic

force microscopy.

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11:20am **AS+MC+SS-FrM10 Energy Loss Of Highly Charged Ions Implanted In MOS Dielectric Films**, ***Radhey Shyam***, *D.D. Kulkarni, D.B. Cutshall, J.E. Harriss, W.R. Harrell, C.E. Sosolik*, Clemson University

Energy loss measurements of highly charged ions in the low kinetic energy regime have been made using as-grown SiO$_2$ (170nm) targets. Highly charged Ar^{+Q} ions (Q=4, 8 and 11) with a kinetic energy of 1 keV were used to produced electronic excitations in the oxides. The irradiated regions of the oxide were then encapsulated under a top metallic contact to form metal-oxide-semiconductor (MOS) devices. The devices were probed with capacitance-voltage (C-V) measurements and the extracted flatband voltages from the C-V curves were correlated with ion energy (kinetic and potential).

The C-V results for highly charged ion experiments reveal that the changes in the flatband voltage and slope for implanted devices relative to the pristine devices can be used to delineate effects due to implanted ions only and ion induced damage. The results confirm that dose as well as and charge-dependent effects can be recorded for irradiation of oxides using this method. In particular, the results as a function of charge state indicate that there is a significant enhancement in the induced flatband voltage shift as the charge state of the beam is increased. This was quantified by measuring the flatband voltage shift across multiple ion doses for fixed incident charge states to obtain a normalized value of the shift induced per incident ion. These normalized results show an enhancement in the shift, which grows monotonically across our charge state data, from 1.14 x 10^{-12} V/ion for Ar^{1+} ions to 1.12 x 10^{-11} V/ion for Ar^{11+} ions. This enhancement in the shift is consistent with the increased potential energy of the higher charge states (e.g. 15 eV for Ar^{1+} and 2004 eV for Ar^{11+}). Viewed as a function of the ion charge state, these data suggest a near-quadratic dependence on the incident charge which is consistent with some theoretical predictions.

Spectroscopic Ellipsometry Focus Topic
Room: 304 - Session EL+AS+BI+EM+SS-FrM

Application of SE for the Characterization of Organic and Biological Materials
Moderator: Tino Hofmann, University of Nebraska-Lincoln

8:20am **EL+AS+BI+EM+SS-FrM1 Multimodal Optical and Mass Spectrometric Imaging of Cells and Tissues**, ***DaeWon Moon***, DGIST, Republic of Korea **INVITED**

Understanding interfacial phenomena has been one of the main research issues not only in semiconductors but only in life sciences. I have been trying to meet the atomic scale surface and interface analysis challenges from semiconductor industries and furthermore to extend the application scope to biomedical areas. Optical imaing has been most widely and successfully used for biomedical imaging but complementary mass spectrometric imaging can provide more detailed molecular specific information

In this presentation, I report our recent activities of multimodal nanobio imaging of cardiovascular cells and tissues. Firstly, in atherosclerotic plaque imaging using coherent anti-stokes raman scattering (CARS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS), multimodal CARS & SIMS analysis showed that increased cholesterol palmitate may contribute to the formation of a necrotic core by increasing cell death. Secondly, surface plasmon resonance imaging ellipsometry (SPRIE) was developed for cell biointerface imaging of cell adhesion, migration, and infiltration dynamics for HUVEC, CASMC, and T cells. SPRIE images were validated with confocal fluorescence microscopy. Collagen fibrils are widely used as cell adhesion substrates. Changes of surface composition and elastic modulus of collagen fibrils after thermal and acidic treatment were investigated by TOF-SIMS and non-contact force microscopy. Multimodal SPRIE & TOF-SIMS imaging would be a useful methodology for understanding cell-substrate interactions in tissue engineering.

In conclusions, multimodal optical and mass spectrometric imaging privides overall structural and morphological information with complementary molecular specific information, which can be a useful methodology for biomedical studies. Future challenges in optical and mass spectrometric imaging for new biomedical applications will be discussed regarding to in-vivo imaging.

9:00am **EL+AS+BI+EM+SS-FrM3 Sum Decomposition of Mueller Matrices from Beetle Cuticles**, ***Hans Arwin***, *R. Magnusson,* Linköping University, Sweden*, E. Garcia-Caurel, A. de Martino,* LPICM-CNRS, Ecole Polytechnique, France*, K. Järrendahl,* Linköping University, Sweden*, R. Ossikovski*, LPICM-CNRS, Ecole Polytechnique, France

Spectral Mueller matrices are very rich in information about physical properties of a sample. We have recently shown that polarizing properties like ellipticity and degree of polarization, can be extracted from a Mueller matrix measured on a beetle cuticle (exoskeleton). Mueller matrices can also be used in regression analysis to model nanostructures in cuticles. Here we present the use of sum decomposition of Mueller matrices from these depolarizing biological reflectors to explore the fundamental character of these reflectors. The objective is to decompose a Mueller matrix into well-defined ideal non-depolarizing matrices corresponding to mirrors, circular polarizers, halfwave retarders etc. Generally it is possible to decompose a measured depolarizing Mueller matrix M into four (or fewer) non-depolarizing matrices according to $\mathbf{M}=\alpha\mathbf{M}_1+\beta\mathbf{M}_2+\gamma\mathbf{M}_3+\delta\mathbf{M}_4$, where α, β, γ and δ are eigenvalues of the covariance matrix of **M**. Two strategies for decomposition will be discussed. A Cloude decomposition will provide the eigenvalues and also the $\mathbf{M}_i$'s although the latter will contain severe noise in some spectral regions. However, a major advantage with the Cloude decomposition is that the number of nonzero eigenvalues is directly obtained, i.e. the number of contributing $\mathbf{M}_i$ matrices. In an alternative decomposition, the $\mathbf{M}_i$'s are assumed and the eigenvalues are found by regression analysis based on **M**. In the case with two non-zero eigenvalues we define a model Mueller matrix $\mathbf{M}_D=\alpha_R\mathbf{M}_1+\beta_R\mathbf{M}_2$ with $\alpha_R+\beta_R=1$. With α_R as adjustable parameter, the Frobenius norm $||\mathbf{M}-\mathbf{M}_D||$ is minimized for each wavelength in the spectral range of **M**. For more complex structures, the regression can be extended by adding more matrices up to a total of four. Advantages with a regression approach are its simplicity and stability compared to a Cloude decomposition. The Mueller-matrix spectra of beetle cuticles are recorded with a dual rotating compensator ellipsometer in the spectral range 400 – 900 nm at angles of incidence in the range 20 - 75°. The application of decomposition on biological reflectors is demonstrated on **M** measured on the beetle *Cetonia aurata*, which represents a narrow-band chiral Bragg reflector with two non-zero eigenvalues. A decomposition in an ideal mirror and a circular polarizer is feasible. In another example, the broad-band and gold-colored beetle *Chrysina* *argenteola*, we show that more than two eigenvalues can be nonzero, especially at oblique incidence, and additional matrices are involved.

9:20am **EL+AS+BI+EM+SS-FrM4 Polymer- and Ceramic-Supported Hybrid Gas Separation Membranes Characterized by Ellipsometry**, ***Ioannis A. Mergos***, *H. Verweij*, The Ohio State University

Membrane structures consist of thin continuous layers deposited on porous ceramic or polymer supports. We have been developing inorganic and hybrid membranes for various applications that include gas separation (e.g. post-combustion CO_2 capture), water purification, Solid Oxide Fuel Cells (SOFC) and sensors. Spectroscopic Ellipsometry (SE) is a major non-destructive characterization tool, which can be used to obtain the thickness (typical range 50 nm…2 μm) and complex refractive index (n,k) of the supported membrane layers. This information, in turn, is used to obtain information about membrane composition, porosity and gas or water sorption. The characterization of fully-ceramic structures on optically smooth porous α-alumina surfaces (roughness ~25 nm, higher than most typical SE applications) has been employed by our group for several years. Recently we have expanded the use of SE to characterization of multi-layered membranes, and of inorganic or polymer layers on polymer supports, on coarser α alumina surfaces, and on ceramic tubes. Examples are γ- and α-alumina on polyethersulfone (PES) and poly-sulfone (PES), $Ce_{0.9}Gd_{0.9}O_{1.95}$ on tubular α-alumina, and successive layers of amorphous microporous silica and polydimethylsiloxane (PDMS) on mesoporous intermediate layers. We have achieved signal detection and interpretation to acquire meaningful results, even in multi-layered structures and in cases with substantial interfacial of surface roughness, or curvature. Overall, the application of SE, including non-destructive characterization at intermediate stages between deposition and processing steps, can significantly facilitate the design of gas separation membrane structures that combine organic and polymer layers.

9:40am **EL+AS+BI+EM+SS-FrM5 Spectroscopic Ellipsometry Methodology for Analysis of Thin Films with Significant Surface Non-idealities: Combining Through-the-Substrate and Film-Side Measurements**, ***Jian Li***, University of Toledo, *L. Mansfield*, National Renewable Energy Laboratory, *P. Pradhan*, University of Toledo, *H. Du, S. Glenn, J. Mann, A. Norman, K. Ramanathan*, National Renewable Energy Laboratory, *R.W. Collins*, University of Toledo, *G. Teeter, D. Levi*, National Renewable Energy Laboratory

Spectroscopic ellipsometry (SE) is a powerful tool for studying thin films, including the thickness and dielectric function, the latter being closely related to important properties such as composition, phase, grain size, porosity, and stress. The sub-nanometer sensitivity of SE is best exploited if all interfaces between layers, at substrate/layer and layer/ambient are abrupt and smooth. Even for the simple structure of substrate/film/ambient, however, whereby the film is fabricated in a uniform process, surface non-idealities including roughness, oxides, compositional variations, or a combination of these, are inevitable. If an accurate film dielectric function is of interest, then the widely-used effective medium approximation (EMA) treatment of the surface roughness can distort the result, especially in photon energy range of strong absorption.

In this work, an improved SE methodology has been developed, tested, and applied to study thin films with significant surface non-idealities. The investigated materials include $Cu(InGa)Se_2$, Zn(O,S), Cu_2ZnSnS_4, and Cu_2SnS_3 deposited on transparent substrates by co-evaporation, sputtering, or chemical bath deposition. The film thicknesses in this study range from ~ 20 to 4000 nm, with potential applicability of the methodology over an even wider range. The key component of the SE methodology is integration of through-the-substrate (TS) SE with standard film-side (FS) SE. The following successes have been demonstrated.

(1) When the surface non-ideality is predominantly roughness within the EMA applicability, two-side (FS+TS) SE can minimize dielectric function distortion caused by the EMA assumptions.

(2) When the surface non-ideality is outside the EMA applicability and traditional SE methodology becomes unreliable, accurate results can be obtained using the FS+TS SE methodology, in which the dielectric functions of the surface and bulk layers can be allowed to vary wavelength by wavelength independently. Most thin films of this study fall into this category.

(3) When the surface is macroscopically rough and scatters light, films can be grown intentionally thick and hence rough enough to suppress specular reflection from the surface. In this case, through-the-substrate SE alone can be used to extract the bulk film dielectric function.

An important criterion for evaluating SE analysis on semiconductor films is that the ε_2 spectrum should be flat and essentially zero below the band gap. It is demonstrated that the dielectric functions obtained through the above SE methodology either satisfy or better satisfy this criterion compared to previous studies. The limitations of the SE methodology will also be discussed.

10:00am **EL+AS+BI+EM+SS-FrM6 A Classical Model for Depolarization through Incoherent Superposition of Dipoles Driven by Evanescent Fields**, ***Kurt Hingerl***, University Linz, Austria

A finite spectral resolution and/or an imperfectly collimated beam /and or an (areal) extended light source / and or an (areal) extended detector and/ or a sample with a varying thickness can produce depolarization effects. However, despite these experimental findings, there are to our knowledge no physical models published which trace the origin of depolarization back to the atomic properties. Therefore, we explain depolarization by the following steps:

1) A mathematical model for cross- polarization: In structured samples the Fresnel reflectances are not correct any more, they rely on homogeneity (i.e. an arbitrary shift of the sample along any surface direction). Mathematicians are aware of this and the numerical tools developed by them, e.g. finite element methods (FEM) or rigorous coupled wave analysis (RCWA), take these effects into account, when matching boundary conditions. Mathematically the Jones matrix then possesses nondiagonal elements. This cross polarization signifies the presence of a totally polarized photon state, but takes into account that p- polarized incoming light creates s- polarized outgoing and vice versa.

2) Cross- polarization then has to take into account radiating dipoles, whose radiation create the scattered cross (and later, after incoherent superposition, partially de-) polarized field. In any structured sample there are inner boundaries present and it is straightforward to show that the usual boundary conditions on the continuity of the tangential electric field and the normal of the displacement field yield inherent contradictions at these inner boundaries. In order to fulfill the boundary conditions, close to the inner boundaries **evanescent fields** must be present, which drive the atomic dipoles in ***other spatial directions than the incoming field.***

3) Depolarization: The end point of the field of unpolarized light may be assumed to move quite irregularly, and the light shows no preferential directional properties when resolved in arbitrary orthogonal directions normal to the direction of propagation. Depolarization is mathematically described by the ***correlation*** which exists between these two orthogonal directions. Furthermore the extension of the light source, the extension of the detector and *the extension of the illuminated sample area* ***(especially its depth!)*** are reducing the value above. The measured intensity at the detector is obtained by the ***incoherent superposition*** of the single waves. The mathematical formulation is given by the Cittert- Zernike theorem (M. Born & E. Wolf, *Principles of Optics*, chapter X.9).

10:40am **EL+AS+BI+EM+SS-FrM8 The Development Of Highly-Oriented 3D Nanostructures For Use With Ultra-Thin Layer Chromatography And Ellipsometry**, ***Erika Pfaunmiller***, University of Nebraska Lincoln, *D. Peev, D. Sekora*, University of Nebraska-Lincoln, *S. Beeram*, University of Nebraska Lincoln, *C. Rice, M. Schubert, T. Hofmann, D. Hage*, University of Nebraska-Lincoln

Slanted columnar thin films based upon SiO_2 were deposited on glass substrates through the use of glancing angle deposition (GLAD). The typical length of these structures was between 500 nm and 2.5 μm. These thin films were then evaluated for use in ultra-thin layer chromatography (UTLC), which is a special type of thin layer chromatography (TLC) that uses supports that incorporate nanomaterials. In this work, a series of lipophilic dyes were analyzed through the use of both TLC and UTLC followed by detection through imaging ellipsometry. It has previously been demonstrated that changes in birefringence is seen as small organic molecules attach to some of the types of nanostructures that were used in this study. The principle behind the detection of organic chemicals that attach/adsorb onto such nanostructures is based on the variation of the optical anisotropy of highly-ordered 3D nanostructures with attached or adsorbed molecules. This causes screening of the dielectric displacement charges that are produced by the incident electromagnetic fields within the nanostructures, which can be measured as a variation of the effective birefringence of the highly-ordered 3D nanostructures. Measurement of this birefringence was done through generalized imaging ellipsometry. This combined imaging and separation approach should be useful for label-free detection in UTLC and for the chromatographic analysis of a various target compounds.

Scanning Probe Microscopy Focus Topic
Room: 312 - Session SP+AS+BI+EM+NS+SE+SS-FrM

Probe-Sample Interactions and Emerging Instrument Formats
Moderator: Carl Ventrice, Jr., University at Albany-SUNY

8:40am **SP+AS+BI+EM+NS+SE+SS-FrM2 2013 ASSD Student Award Talk: New Insights into Nanoscale Adhesion from *In Situ* TEM Studies**, ***Tevis Jacobs***, *J.A. Lefever,* University of Pennsylvania*, J. Liu,* University of Wisconsin-Madison*, D.S. Grierson,* SysteMECH LLC*, K.E. Ryan, P.L. Keating, J.A. Harrison,* United States Naval Academy*, K.T. Turner, R.W. Carpick*, University of Pennsylvania

A fundamental understanding of adhesion is important for applications at all length scales, but is particularly critical in nanoscale devices and applications due to their high surface-to-volume ratio. Advancements in studying such tribological phenomena are typically hindered by the inaccessibility of the sliding interface. We will present nanoscale adhesion measurements conducted inside of a transmission electron microscope (TEM), using a modified in situ nanoindentation apparatus that makes contact with atomic force microscope (AFM) cantilever tips. This tool provides new opportunities to observe, identify, and quantify tribological processes with unprecedented access and resolution. First, using ultra-strong carbon-based tip materials, we find that roughness of tips can greatly reduce the pull off force and lead to severe underestimation of the work of adhesion [1]. Furthermore, we have quantified adhesion by making and breaking contact between nanoscale silicon asperities and a flat diamond substrate. The snap-in distance and the pull-off force are measured with sub-nanometer and sub-nanonewton resolution, respectively. The shape of the Si asperity is determined with sub-nanometer resolution immediately before and after contact to verify that elastic conditions were maintained. From this, we independently determine the work of adhesion and range of adhesion. The results show that accounting for roughness has a strong effect on both parameters. These two results demonstrate the importance of applying in situ approaches to studies of adhesion. --- 1. Jacobs, T.D.B., Ryan, K.E., Keating, P.L., Grierson, D.S., Lefever, J.A., Turner, K.T., Harrison, J.A. and Carpick, R.W. The Effect of Atomic-Scale Roughness on the Adhesion of Nanoscale Asperities: A Combined Simulation and Experimental Investigation. Tribol. Lett. 50, 81-93 (2013).

9:40am **SP+AS+BI+EM+NS+SE+SS-FrM5 Nanoscale Mapping of the W/Si(001) Schottky Barrier using Ballistic Electron Emission Microscopy**, ***Christopher Durcan***, University of Albany-SUNY*, V.P. LaBella*, University at Albany-SUNY

The W/Si(001) Schottky barrier was spatially mapped using ballistic electron emission microscopy (BEEM) and ballistic hole emission microscopy (BHEM) using high resistivity *n*-type and *p*-type silicon substrates. A thin tungsten silicide is observed upon deposition utilizing transmission electron microscopy (TEM) and Rutherford backscattering spectrometry (RBS). The sum of the Schottky barrier heights from *n*-type and *p*-type silicon substrates agree with the silicon band gap. The BEEM and BHEM spectra are fit utilizing a linearization method to the power law of the BEEM model. Spatially resolved Schottky barrier maps are generated over a 1μm x 1μm area and provide insight into the spatial homogeneity of the barrier height. Histograms of the barrier heights show a Gaussian distribution, consistent with an interface dipole model.

10:00am **SP+AS+BI+EM+NS+SE+SS-FrM6 Local Probing of Superconductivity in Half Heusler Compounds**, ***Hongwoo Baek***, NIST & Seoul National University, Republic of Korea*, J. Ha, D. Zhang,* NIST/Maryland Nano Center, University of Maryland*, Y. Nakajima, P.S. Syers, X. Wang, K. Wang, J. Paglione,* University of Maryland*, Y. Kuk,* Seoul National University, Republic of Korea*, J.A. Stroscio*, NIST

Heusler alloys have attracted interest as multifunctional experimental platforms for topological quantum phenomena ranging from magnetism to superconductivity and heavy fermion behavior. The rare-earth chalcogenide ternary half Heusler compounds were theoretically predicted to have topologically nontrivial surface states due to band inversion [1]. The lack of inversion symmetry of the crystal lattice makes unconventional pairing symmetry feasible. The superconductivity in the non-centrosymmetric half Heusler compound YPtBi was recently reported as a promising system for the investigation of topological superconductivity [2]. In this work, we use ultra low temperature scanning tunneling micro scopy to investigate the superconducting properties of the ternary half Heusler compounds YPdBi and YPtBi. Both were theoretically proposed to have topological states with different band inversion strength [1], and experimentally reported as a topological insulator [3]. Strong spin-orbit coupling and the lack of inversion symmetry present the possibility of spin-triplet superconductivity in these materials. T he tunneling spectra of YPdBi show two different superconducting gaps of 0.36 meV and 0.16 meV depending on the measurement location. The variation in gaps might originate from inhomogeneity in the crystal. The superconducting gap of 0.36 meV is completely suppressed above a critical magnetic field of B=2.5 T, in agreement with bulk transport measurements. A superconducting gap of 0.21 meV and an upper critical field of 1.25 T were measured in a circular superconducting domain of diameter ≈180 nm in YPtBi. Sequential addition of single vortices to the superconducting YPtBi domain could be observed with increasing magnetic field, with vortices occupying the perimeter of the island. These observations will be discussed in terms of island confinement and pairing symmetry of YPtBi.

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10:40am **SP+AS+BI+EM+NS+SE+SS-FrM8 Multimodal Intermittent Contact Atomic Force Microscopy: Topographical Imaging, Compositional Mapping, Subsurface Visualization and Beyond**, ***Santiago Solares***, George Washington University

Multifrequency atomic force microscopy (AFM) refers to a family of techniques that involve excitation of the microcantilever probe at more than one frequency [R. Garcia and E.T. Herruzo, Nature Nanotechnology 7, 217 (2012)]. This can be carried out in a sequential manner, varying the excitation frequency over time, as in chirp band excitation methods, or simultaneously supplying drive signals containing more than one frequency to the cantilever shaker. The latter mode of operation commonly involves the simultaneous excitation of more than one cantilever eigenmode, such that each eigenmode is used to carry out different functions. For example, in a recently developed trimodal imaging scheme for soft sample characterization [D. Ebeling, B. Eslami and S.D. Solares, ACS Nano, 7, 10387 (2013)], the fundamental eigenmode is used for topographical acquisition, as in standard tapping-mode AFM, while two higher eigenmodes are used for compositional mapping and subsurface visualization, respectively. This talk presents experimental and computational results for validated multimodal imaging schemes involving one to three eigenmodes, and discusses the expected benefits and complexities of including more than three eigenmodes.

Surface Science
Room: 309 - Session SS+EM-FrM

Semiconductor Surfaces and Interfaces 2
Moderator: Robert Bartynski, Rutgers, the State University of New Jersey, Kurt Kolasinski, West Chester University

8:20am **SS+EM-FrM1 Two Dimensional Supramolecular Ordering of Oligothiophene Molecules on the Si(111) $\sqrt{3}\times\sqrt{3}$-Ag Surface**, *R. Liu,* Lakehead University, Canada*, C. Fu, D.F. Perepichka,* McGill University, Canada, ***Mark Gallagher***, Lakehead University, Canada

The functionalization of semiconductor surfaces with organic molecules is a necessary step in the development of hybrid organic-semiconductor structures. A significant challenge to organic layer formation is the fact that semiconducting surfaces exhibit a large number of dangling bonds, which suppress the diffusivity of adsorbed molecules and can even break the molecules apart via the formation of Si-C bonds. Recently it has been shown that these problems can be obviated by depositing the organic molecules onto a passivated surface [1].

We have studied the adsorption of brominated π conjugated tetrathienoanthracene molecules (TBTTA) onto the Si(111)-$\sqrt{3}\times\sqrt{3}$-Ag surface. Thiophene based molecules like TBTTA are of considerable interest in organic semiconductor research due to their efficient conjugation and the chemical stability [2]. The Si(111) $\sqrt{3}\times\sqrt{3}$-Ag surface has no Si dangling bonds and should provide a high mobility surface suitable for TBTTA adsorption. Scanning Tunneling Microscopy images reveal that at low coverage the molecules readily migrate to step edges and defects in the $\sqrt{3}$ overlayer, in fact many images show direct evidence of molecular mobility. With increasing coverage the molecules eventually form compact supramolecular structures. In terms of the $\sqrt{3}$ lattice vectors ($\boldsymbol{a}$ and $\boldsymbol{b}$), the oblique unit cell of these structures is $\boldsymbol{a}_m = 3\boldsymbol{a} + \boldsymbol{b}$, and $\boldsymbol{b}_m = \boldsymbol{a} + 2\boldsymbol{b}$. The structures are quite fragile and can decompose under repeated STM imaging. Our results suggest that TBTTA is weakly bound to the $\sqrt{3}$ surface at room temperature and that the supramolecular structures are held together by weak van der Waals forces.

1. T. Suzuki et al., Phys. Chem. Chem. Phys. 11, 6498 (2009).

2. R. Gutzler et al., Nanoscale 6, 2660-2668 (2014).

8:40am **SS+EM-FrM2 Interface Formation between a Self-Assembled Monolayer and an Organic Semiconductor**, ***Sujitra Pookpanratana**, H.-J. Jang, A.N. Brigeman, J.I. Basham, O.A. Kirillov, D.J. Gundlach,* National Institute of Standards and Technology (NIST)*, O.D. Jurchescu,* Wake Forest University*, C.A. Richter, C.A. Hacker*, NIST

Organic-based electronics are attractive because they have potential manufacturing advantages such as mechanical flexibility and simpler processing (solution-based, low temperature, and atmosphere conditions). Molecular-based semiconductors offer a nearly limitless range of possibilities in tailoring the chemical composition and structure for a desired electronic, optical, or film-processing property. Probing and understanding molecular surfaces and interfaces is essential for the further development of organic-based photovoltaics, light emitting diodes, and field-effect transistors. Organic-organic interfaces are key in some of those devices, and understanding the impact of a self-assembled monolayer (SAM) has when an organic semiconductor is on top of it, is a complex issue.[1] This strategy is commonly implemented as a way to modify the hole injection barrier between an organic material and an inorganic substrate.

Here, we have investigated the interaction between a pi-conjugated organic semiconductor (tris-(8-hydroxyquinoline) aluminum, Alq_3) on SAM's of different tail and backbone composition. We have used ultraviolet and X-ray photoelectron spectroscopies to monitor the energy level alignment and chemical structure at the interface. The SAM's strongly interact with the Au substrate, where an interface dipole can down shift or up shift the surface work function. After Alq_3 is deposited onto the SAM-coated substrates, we find that the highest occupied molecular orbital of Alq_3 is relatively constant (with respect to the substrate Fermi level) on all surfaces, suggesting Fermi level pinning.[2] However, the composition of the SAM's did strongly influence the growth and chemical structure of the Alq_3 at the interface. The photoemission signal arising from the Au substrate is least attenuated when the SAM/Au surface is hydrophobic when compared to a hydrophilic SAM/Au or bare Au surface. The difference in substrate attenuation suggests that that the early growth of the Alq_3 layer strongly depends on this surface property. This finding is corroborated with microscopy of the same samples. In addition, Alq_3 chemically reacts with a fluorinated SAM at the organic-organic interface as indicated by the shifting and asymmetric broadening of Al and N core levels. These results will be discussed in context of painting a comprehensive picture of the organic-organic interface formation that influences the chemical composition, electronic structure and physical structure at the interface.

[1] F. Rissner *et al*, *ACS Nano* 3, (2009) 3513.

[2] L. Lindell *et al*., *Appl. Phys. Lett*. 102, (2013) 223301.

9:00am **SS+EM-FrM3 Reactions of Benzoquinone with Hydrogen Terminated Silicon Surfaces**, *R.L. Opila, **Meixi Chen**, N.A. Kotulak, N.J. Schreiber*, University of Delaware

Quinhydrone dissolved in methanol has long been know to react with hydrogen terminated silicon surfaces to passivate electronic defects where photo-excited carriers recombine non-radiatively. The mechanism of this passivation is not well understood. We have shown that benzoquinone, $C_6O_2H_4$ rather than hydroquinone, $C_6O_2H_6$, both components of the quinhydrone mixture, is the active component. Benzoquinone reacts to abstract a hydrogen and then itself bonds with the surface. We have shown that the hydrogen can be abstracted from the solvent and that incident light is necessary for this reaction to take place. X-ray photoelectron spectroscopy and Fourier Transform Infrared Spectroscopy were used to show that the benzoquinone reacted with the surface. Photo-excited carrier lifetime is a good measure of the extent of the passivation of the surface. Density functional theory supports the proposed reaction mechanism.

9:20am **SS+EM-FrM4 High-Quality Monolayers Derived from Short Alkyne Chains on Si(111) Surfaces**, ***Sidharam Pujari**, A. Filippov, S. Gangarapu, H. Zuilhof*, Wageningen University, Netherlands

Hydrosilylation has been a key reaction in preparing monolayers on silicon surfaces. This process involves the reaction of a terminally unsaturated reactant with the Si surface. Over the past 20 years, several advances have been accomplished to obtain better (i.e. denser and more stable) monolayers with various reactants (alkenes, alkynes, dienes, etc.) under different reaction conditions (e.g. thermal initiation, ultraviolet light, etc.).[1,2] Such a higher density is advantageous for the structural ordering, stability and a wide range of applications. The procedure used in our lab (as well as labs around the world) involves wet-chemical techniques for the surface modifications. As the name implies, the reactants with these techniques must be available as liquids under the reaction conditions. Due to this constraint, only monolayers of relatively long chain lengths have been made, because shorter chains evaporate under thermal conditions (or are even a gas). In the current project, we have prepared and characterized a new class of monolayers with (short) chain lengths that were previously inaccessible.

H-Si(111) surfaces were modified with gaseous alkynes in a pressure-resistant PARR reactor. This novel method in silicon-carbon chemistry allows the chemisorption of compounds that were previously unusable in surface modification due to its volatility. Si–C-bonded monolayers derived from propyne, 1-butyne and 5–functionalized-pent-1-ynes (-COOH, -Cl, & $-NH_2$) were prepared and characterized using various surface-sensitive techniques. Si(111)–propenyl and butenyl silicon-monolayers display a higher packing density (up to 75%) than any wet-chemically prepared alkyne-derived monolayer. Furthermore, a combination of experimental and theoretical data shows that propyne chemisorption happens in a temperature-dependent manner, not observed for any other alkyne studied up to now: through addition of the second carbon (*-iso*) at temperatures below 90 ° C, and of the terminal carbon (*-lin*) above 90 ° C. Finally, 5-chloro-1-pentyne and 4-Pentynoic acid were shown to bind at high surface densities and (near-)exclusively via the terminal carbon of the triple bond. These end groups allow for further functionalization of the monolayer.

(1) Rijksen, B.; Pujari, S. P.; Scheres, L.; van Rijn, C. J. M.; Baio, J. E.; Weidner, T.; Zuilhof, H. *Langmuir***2012**, *28*, 6577-6588.

(2) Li, Y.; Calder, S.; Yaffe, O.; Cahen, D.; Haick, H.; Kronik, L.; Zuilhof, H. *Langmuir***2012**, 9920-9929.

9:40am **SS+EM-FrM5 Surface Modification of Antimonide-Based Compound Semiconductor Superlattices using ALD**, ***Erin Cleveland**, J. Nolde, C. Canedy, E. Aifer*, Naval Research Laboratory

The use of dielectric films in device passivation is complicated by the fact that they are typically deposited on processed material surface that bear little resemblance to that of the virgin growth surface. This is particularly evident in technologically important device structures employing antimonide-based compound semiconductor (ABCS) superlattices, where the exposed mesa sidewalls may be comprised of four or more atomic species and their complex oxides. Physically, the etched surface presents a different crystallographic orientation, and may have additional structure due to variation in etch rate of superlattice layers. Since the nature of the dielectric/semiconductor interface directly impacts the density of surface states, it is critical to understand how processed, multilayer semiconductor surfaces may be modified during the initial phase of the atomic layer deposition (ALD) process.

A significant effort has been focused on surface preparations prior to ALD that removes the native oxide and passivates the III-V atoms in order to ensure the best possible interface. Current approaches typically rely upon wet-chemical etches to remove the defect-prone native oxide layer prior to dielectric deposition; however, this technique typically suffers from a lack of reproducibility, as well as potential interface contamination between processing steps. Therefore, we studied the effectiveness of using the ALD precursor, TMA, in conjunction with wet and dry pre-treatments, in removing carbon and etch precipitates, scavenging the various oxide species, and residues of excess group III and V elements on (100) surfaces of ABCS superlattices as a function of precursor choice, sequence (i.e. TMA vs oxidizer first), exposure time, as well as substrate temperature. Furthermore, surface passivation stability was investigated as a function of temperature and time. Surfaces were analyzed using XPS, AFM, and SEM both before and after ALD treatments. Results indicate that a completely oxide free surface may not be necessary to produce a good electrical interface.

10:00am **SS+EM-FrM6 Mechanism Changes Caused by Metal Catalyst During Silicon Etching in V_2O_5 + HF Solutions**, ***Kurt Kolasinski**, W.B. Barclay*, West Chester University

Etching of Si in oxidant + HF solutions can lead to a self-limiting reaction that spontaneously produces nanocrystalline porous Si – a process known as stain etching. The presence of a metal catalyzes and localizes etching such that ordered arrays of pores or nanowires can be formed depending on the structure of the metal – a process known as metal assisted etching (MAE). Ag, Au, Pd and Pt were deposited from solution onto H-terminated Si to act as catalysts for MAE. The metals all catalyzed the injection of holes into the Si. They all increased the rate of hole injection by approximately a factor of 5. The stoichiometry of MAE in V_2O_5 + HF solutions depended on the chemical identity of the metal. The stoichiometry when etching with Ag and Au was the same as for stain etching in V_2O_5 + HF solutions. However, for Pd and Pt, the stoichiometry differed significantly, consuming more V_2O_5 and producing less H_2 per mole of Si etched. This indicates that the metal catalyst can change the mechanism of etching. Etching in V_2O_5 + HF solutions was well behaved and gave consistently reproducible kinetic results. The behavior is much different when HOOH is added instead of V_2O_5. In the absence of deposited metal, no reaction occurs with HOOH. When HOOH was added to metal-coated Si samples immersed in HF(aq), etching was immediate in all cases. In contrast to V_2O_5, we were unable to obtain well-behaved stoichiometric results for HOOH + HF solutions. This is related to heightened sensitivity on reaction conditions compared to the V_2O_5 system as well as nonlinearities introduced by side reactions.

The mechanism of Si etching changes based on the presence of a metal catalyst during metal assisted etching and depends on the chemical identity of the metal. A valence 2 path dominates the formation of photoluminescent nanoporous Si in stain etching as well as MAE with Ag and Au. A valence 4 path dominates the formation of photoluminescent nanoporous Si in MAE with Pt. However for MAE with Pd, no nanoporous Si is formed initially and a mixture of valence 4 and valence 2 processes is observed. The nature of the electron transfer process and its dependence on the electronic structure of the metal/Si interface will be discussed.

10:40am **SS+EM-FrM8 Selective Wet Etching of III-V Semiconductors with HCl, H_2O_2, and α-Hydroxy Acid Mixtures**, ***Pablo Mancheno-Posso***, *R. Jain, A.J. Muscat*, University of Arizona

The higher electron mobility of III-V semiconductors makes them suitable for NMOS devices in CMOS transistor technology. A clean, smooth and well-defined semiconductor surface is needed for epitaxial growth of heterostructures and atomic layer deposition of dielectrics. Device fabrication also requires selective etching and smooth finishing of layers composed of different materials. Wet chemical treatments enable batch processing, and aqueous mixtures containing an oxidizing agent and an etchant (acid or base) have been developed for III-V materials. The (100) face of the binary III-V semiconductors contains both group III (electron-deficient) and V (electron-rich) atoms. HCl solutions favor the removal of the latter. The addition of α-hydroxy acids (citric and tartaric acids) to the etching mixture is expected to promote a more uniform etch by chelating the group III atoms. In this study, we compare the etching rates of the (100) faces of GaAs, InAs, InP, InSb and GaSb, using aqueous solutions of HCl (0.01-4 M), H_2O_2 (0.01-8 M), and tartaric and citric acids (0.1-1.5 M). The etching rate was determined by profilometry measurements of the step height on patterned substrates. The chemical composition of the surface was studied using XPS, and the surface topography and roughness were characterized with AFM. The etching rate of GaAs in HCl-H_2O_2 mixtures was independent of HCl concentration (0.1-4 M) and showed a linear dependence on H_2O_2 concentration (0.1-8 M). Etching was limited by the removal of water-soluble Ga and As chlorides formed from GaAs oxides. InP etching was independent of HCl concentration (1-5 M), but sharply increased for 6-7 M. H_2O_2 concentration showed no significant effect on InP etching. The GaSb etching rate depended linearly on H_2O_2 concentration but in a narrower range (0.1-0.5 M). The etching of InP and GaSb is limited by the removal of the group III atoms. Etching of GaAs and InAs is limited by the removal of the group V atom. The strong bond that As makes with O drives etching. The etching selectivity of GaAs to InP increased from about 15 to 250 when the H_2O_2 concentration was raised from 1 to 8 M at a fixed 1.76 M HCl concentration. The addition of tartaric or citric acid to HCl and H_2O_2 mixtures yielded no change in the etching rate of GaAs when compared to solutions containing HCl and H_2O_2 only, but preferentially removed Ga atoms, yielding smoother surfaces at low concentrations. Using a chelator etched InAs with high selectivity relative to InP without as much roughening as with HCl. Selective etching will be discussed in the context of a set of proposed mechanisms based on the data.

11:00am **SS+EM-FrM9 Lanthanum Quantification for Optimization of Advanced High-k/Metal Gate Stacks using Low Energy Electron X-ray Emission Spectrometry**, *E. Martinez,* CEA, LETI, MINATEC Campus, France*, C. Trouiller,* STMicroelectronics, France*, M.P. Moret, N. Morel,* CAMECA, France, ***Andrew Davis***, CAMECA Instruments Inc*, P. Caubet,* STMicroelectronics, France*, F. Bertin*, CEA, LETI, MINATEC Campus, France

We report about accurate monitoring of ultra-low La doses inserted in advanced high-k/metal gate stacks for threshold voltage tuning purposes. Three characterization techniques are implemented for precise and reproducible lanthanum quantification. LEXES (Low energy Electron X-ray Emission Spectrometry) capabilities are highlighted in terms of sensitivity and accuracy thanks to a comparison with reference results obtained by Rutherford Backscattering Spectrometry (RBS). The capabilities of state-of-the-art Auger nanoprobes for depth profiling in the sub-nanometer range are also illustrated.

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