Monday Morning, November 10, 2014

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).

Applied Surface Science
Room: 316 - Session AS+MC-MoM

Quantitative Surface Analysis
Moderator: James A. (Tony) Ohlhausen, Sandia National Laboratories, William Stickle, Hewlett Packard

8:20am **AS+MC-MoM1 Automating Multi-Technique Surface Analyses for Materials Characterisation**, ***Andrew Wright***, *P. Mack, T.S. Nunney, A. Bushell, A. Yeadon*, Thermo Fisher Scientific, UK

X-ray photoelectron spectroscopy (XPS) is a well-established technique that has become a cornerstone of surface analysis due to the wealth of chemical bonding information that it provides. Many other surface sensitive techniques exist, of course, and often can be found on the same instrumentation. Ultraviolet photoelectron spectroscopy (UPS) provides detailed valence electronic structure information. Reflection electron energy loss spectroscopy (REELS) can yield hydrogen quantification, shake-up transition and band gap information. Ion scattering spectroscopy (ISS) offers the most surface-sensitive probe of composition. Auger electron spectroscopy (AES) offers chemical information with high spatial resolution. In addition, monatomic and cluster ion beams can be used in concert with these methods for cleaning or depth profiling.

The various techniques can each provide important information in isolation, but the real power of surface analysis comes from combining these analyses of a sample and correlating the information to provide a more thorough characterisation of the material. Traditionally, however, switching between techniques has been difficult or laborious, and this has tended to deter analysts from performing multitechnique studies. Improvements to automation and usability are vital for bringing the less-used methods into common practice.

This paper presents several multitechnique surface analyses of samples in a single instrument (the Thermo Scientific Escalab250Xi) , showing how automated, sequential applications of these complementary chemical, electronic and structural characterisation methods can be applied to polymeric, catalyst, photovoltaic and semiconductor materials, yielding valuable results with minimal effort.

8:40am **AS+MC-MoM2 The *S'* component in the Si 2*p* X-ray Photoemission Spectrum of Si [001]**, ***Alberto Herrera-Gomez***, CINVESTAV-Queretaro, Mexico, *M.O. Vazquez-Lepe,* Universidad de Guadalajara, Mexico, *P.G. Mani-Gonzalez,* Universidad Autónoma de Ciudad Juárez, Mexico, *O. Ceballos-Sanchez*, CINVESTAV-Queretaro, Mexico

Because of the technological relevance of the Si [001] surface, the Si 2*p* is one of the most studied core levels with laboratory X-Ray Photoelectron Spectroscopy (XPS). An important application is the quantification of the thickness of oxide layer, which is done by comparing the intensity of the substrate and Si^{4+} components. Peak-fitting is usually done by employing one doublet for the substrate and another for the Si^{4+} shifted around 3.5 or 4 eV to higher binding energy (from the substrate). In detailed studies, the quantification of the suboxides is usually done employing components, originally proposed by Himpsel et al.,[1] with the following shifts: 2.5 eV for Si^{3+}, 1.75 eV for Si^{2+}, and 0.95 eV for Si^{1+}. A proper fit, besides those five components, actually requires a six component shifted by approximately 0.3 eV. This peak has been clearly identified in various synchrotron studies such as that by Landemark et al.,[2] where it is referred as *S'*. In that study, and in others, it is assigned to one monolayer (the second) of the substrate. Although clearly present in Si 2*p* spectra obtained with laboratory XPS equipped with monochromatized Al Kα radiation, this component is largely unspoken in the literature. In one of the few studies that mention its existence it is assigned to an asymmetry of the bulk peak.[3] In this presentation it is going to be shown that this interpretation is inconsistent with the angular dependence observed by *S'*. The physical origin of *S'*, which is going to be discussed in detail, goes in a direction compatible with that proposed by Landemark et al.: although it represents one monolayer for the clean Si [001] surface, for oxide-covered surfaces it corresponds to a few monolayers of the substrate.

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9:00am **AS+MC-MoM3 Quantitative Analysis of Nanostructured Surfaces by means of X-ray Photoelectron Spectroscopy: Theory and Applications**, ***Wolfgang Werner***, Vienna University of Technology, Austria **INVITED**

The theory of signal emission in electron spectroscopy is discussed on the basis of the so-called Landau-Goudsmit-Saunderson (LGS) loss function, which leads in a natural way to rigorous spectrum analysis techniques, the so--called partial intensity analysis (PIA). Examples of applications include theoretical calculation of model spectra as well as analysis of experimental spectra using of X-ray Photoelectron Spectroscopy (XPS) and Reflection Electron Energy Loss Spectroscopy on nanostructured surfaces [1], the contribution of in-vacuo electron scattering to electron spectra [2] and secondary electron–electron energy loss coincidence spectroscopy (SE2ELCS) [3]. In the latter technique correlated electron pairs are analysed and detected, thereby giving unique insight into the dielectric properties of a solid.

A layered electron gas system will be considered as an important case study for quantitative surface analysis: it is shown how single layer graphene data can be extracted from measurements on macroscopic three dimensional highly oriented pyrolithic graphite (HOPG) samples. After appropriate analysis, a feature in the spectrum can be identified which quantitatively correlates with the sp2-content in arbitrary carbon samples, as follows from comparison with Raman measurements.

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9:40am **AS+MC-MoM5 Effective Attenuation Lengths for Hard X-ray Photoelectron Spectroscopy (HAXPES)**, *A. Jablonski,* Polish Academy of Sciences, Poland, ***Cedric Powell,*** National Institute of Standards and Technology (NIST), *S. Tanuma*, National Institute for Materials Science (NIMS), Japan

HAXPES is now being used to characterize thicker overlayer films than is possible with conventional XPS using Al and Mg Kα x-ray sources. As a result, there is a need for effective attenuation lengths (EALs) to determine film thicknesses at electron energies larger than about 1.5 keV. Jablonski and Powell [1] published a simple practical EAL expression from fits to EALs calculated from solution of the kinetic Boltzmann equation within the transport approximation for electron energies between 61 eV and 2 keV and photoelectron emission angles between 0° and 50°. This approach has now been extended to electron energies up to 5 keV with account also taken of non-dipole terms in the photoionization cross section. EALs have been calculated for Si 1s, Cu $2p_{3/2}$, Ag $3d_{5/2}$, and Au $4f_{7/2}$ photoelectrons excited by Mg Kα, Al Kα, Zr Lα, and Ti Kα x rays using the inelastic mean free paths of Tanuma *et al*. [2] for each solid. EALs from the non-dipole approximation were up to about 2% larger than those from the dipole approximation. Good agreement has been found between the new EALs and EALs determined from Monte Carlo simulations and from the NIST SESSA database [3]; with the latter database, simulations can be made for photoelectron energies up to 20 keV. We found that the new EALs were also consistent with the previous expression [1]. Finally, the new EALs are reasonably consistent with the EALs measured by Sacchi e*t al*. [4] for Co, Cu, and Ge but there was poorer agreement with the EALs measured by Rubio-Zuazo and Castro [5] for Au. Disagreements between the calculated and measured EALs for Au at energies less than 5 keV were attributed to non-ideal morphologies of the thinner Au films.

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10:00am **AS+MC-MoM6 Angle-Resolved XPS Test Structures Fabricated *In Situ* by Argon Ion and Argon Cluster Ion Treatment**, ***Peter Cumpson***, *A.J. Barlow, J.F. Portoles, N. Sano*, Newcastle University, UK

Nondestructive depth-profiling by inversion of Angle Resolved XPS spectra[1] has been a desire in the XPS community for a long time. The lack of reference specimens with known structures has been a severe handicap in the development of the technique. Until now, reference materials with known depth-profiles have largely been confined to thin oxide layers on aluminium or silicon, and even these have uncertain carbon contamination layers. Progress has been made, though, with depth-profiling numerical methods[2] that need comparison with real known structures. It is difficult to fabricate structures with nanometre-scale variation in concentration with depth, and even more difficult to transport them without contamination (and the potentially damaging removal of such contamination).

We have developed protocols for the fabrication of two different samples, one organic and the other inorganic, with known depth-profiles *in situ* in XPS instruments;

Glancing-angle monatomic argon sputtered PEDOT:PSS, a common conducting polymer blend, and

Argon cluster-ion sputtered indium arsenide (InAs), a compound semiconductor

Indium arsenide and PEDOT:PSS are both widely-available, almost atomically flat and sufficiently electrically conductive to ensure no sample charging occurs. Glancing angle monatomic sputtering of PEDOT:PSS leaves a PEDOT enhanced region at the surface, the spatial parameters of which depend only on sputter ion conditions under direct experimental control. Recently we have demonstrated the unexpected result that argon gas-cluster sputtering of InAs results in a thin, coherent metallic indium layer at the surface[3], the basis for InAs reference material structure.

The ill-posed nature of the inversion of ARXPS data means it is sensitive to small experimental uncertainties. We apply three different ARXPS algorithms, including regularization, to the data from these in situ reference structures. This gives a set of reference data that will allow comparison with results from any XPS work following the same preparation protocol. This should greatly improve confidence in the results of ARXPS depth-profiling.

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10:40am **AS+MC-MoM8 Metrology for Surface Chemical Analysis: Active Parties, Status and Challenges**, ***Wolfgang Unger***, BAM Federal Institute for Materials Research and Testing, Germany

The International Bureau of Weights and Measures (BIPM) defines metrology, i.e. the *Art of Measurement*, as "the science of measurement, embracing both experimental and theoretical determinations at any level of uncertainty in any field of science and technology." Besides the establishment of full uncertainty budgets traceability is another aspect of metrology.

Surface chemical analysis is a much younger discipline in comparison to other branches in analytical chemistry as, e.g., electro-chemistry, inorganic and gas analysis and lots of work has to be done to make XPS, AES and SIMS based quantitative analysis a metrological one. Looking to the analytical methods established in surface chemical analysis we may differentiate classes:

1. Primary methods measuring amount of substance as [atoms/cm^2, …]

2. Empirical methods measuring amount of substance after calibration as fractions of a nano scaled surface layer

3. Primary and empirical methods measuring amount of substance expressed as the thickness of a thin film [nm]

In most cases we are using empirical methods when XPS, AES and SIMS are applied to deliver quantitative data. It follows also from that list that, principally, traceability to the mol or the meter can be established.

Relevant initiatives to metrologically underpin surface chemical analysis have been launched under the umbrella of the Surface Analysis Working Group at CCQM/BIPM where the National Metrology Institutes are running world-wide inter-laboratory comparisons. In Europe we have the European Metrology Research Program (EMRP) where a number of projects directly address issues of surface chemical analysis and most often also by individual websites. Another aspect is that there is a strong impact of metrology in surface chemical analysis on standardization in ISO TC 201 and 202. For example, ISO 14701 has been prepared using outcome of a huge key comparison organized under CCQM/BIPM.

The talk will present some basics of metrology in surface chemical analysis, results of successful key comparisons organized under CCQM/BIPM and a survey on the main scientific challenges to be addressed in quantitative surface chemical analysis in the next future.

11:00am **AS+MC-MoM9 Local Crystallography: Phases, Symmetries, and Defects from Bottom Up**, *A. Belianinov, Q. He, A,. Borisevich, S. Jesse, **Sergei Kalinin***, Oak Ridge National Laboratory

Progress in high-resolution real space imaging techniques such as (Scanning) Transmission Electron Microscopy (STEM) and Scanning Tunneling Microscopy (STM) has allowed high veracity, direct imaging of atomic columns (STEM) and surface atomic structures. While the data acquisition platforms are continuously evolving, the basic data processing principle - analysis of structure factor, or equivalently two point correlation function averaged over probing volume – remained invariant since the early days of Braggs. We propose an approach based on the multivariate statistical analysis of the coordination spheres of individual atoms to reveal preferential structures and symmetries. The underlying mechanism is that for each atom, *i*, laying on the lattice site with indices (*l, m*), we construct a near coordination sphere as a vector $\mathbf{N}_i = (x_1,..., x_8)$, where $(x_j, y_{j+1})$is the radius-vector to *j/2*-th nearest neighbor. Once the set of $\mathbf{N}_i$ vectors is assembled, its statistical properties are analyzed though cluster analysis and various multivariate methods to reveal and extract regions of symmetry, distortions, different phases, boundaries, defects, etc. Results are presented on various model and real material systems including $La_{0.7}Sr_{0.3}MnO_3$, $BiFeO_3$, $LaCoO_3$ and discussed in light of physical parameter extraction.

Acknowledgement:

Research for (AB, QH, AB, SJ, SVK) was supported by the US Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division. Research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, US Department of Energy.

11:20am **AS+MC-MoM10 Chemical Warfare Agent Surface Adsorption: Hydrogen Bonding of Sarin and Soman to Amorphous Silica**, ***Erin Durke**, W.O. Gordon,* Edgewood Chemical Biological Center*, A.R. Wilmsmeyer,* Augustana College*, D. Troya, J.R. Morris*, Virginia Tech

Sarin and soman are warfare nerve agents that represent some of the most toxic compounds ever synthesized. The extreme risk in handling such molecules has, until now, precluded detailed research into the surface chemistry of agents. We have developed a surface science approach to explore the fundamental nature of hydrogen bonding forces between these agents and a hydroxylated surface. Sarin and soman are deposited via a directional doser onto an amorphous silica surface and characterized by reflection-absorption infrared spectroscopy (RAIRS) in an ultra-high vacuum (UHV) chamber. Once the chemical agent coverage reached monolayer values, temperature programmed desorption is performed to determine the binding energy. Changes in the OH region of the IR spectra are monitored in real time with RAIRS, and the degree of shift in the H-bonded OH peak shows a linear relationship with the strength of the interaction between agent and silica surface. Infrared spectroscopy revealed that both agents adsorb to amorphous silica through the formation of surprisingly strong hydrogen-bonding interactions with primarily isolated silanol groups (SiOH). Comparisons with previous theoretical results reveal that this bonding occurs almost exclusively through the phosphoryl oxygen (P=O) of the agent. Temperature-programmed desorption experiments determined that the activation energy for hydrogen bond rupture and desorption of sarin and soman was 50 ± 2 kJ/mol and 52 ± 2 kJ/mol, respectively. X-ray photoelectron spectroscopy (XPS) is also used to confirm molecular desorption of the agents from the silica substrate. Together with results from previous studies involving other phosphoryl-containing molecules, we have constructed a detailed understanding of the structure-function relationship for nerve agent hydrogen bonding at the gas-surface interface.

11:40am **AS+MC-MoM11 The Shake-up Satellites in the Fe 2*p* Core Level X-ray Photoelectron Spectra Analyzed with the Double Lorentzian Line Shape**, ***M. Bravo-Sanchez**,* CINVESTAV-Queretaro, Mexico*, J.A. Huerta-Ruelas,* Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada, Mexico*, A. Herrera-Gomez,* CINVESTAV-Queretaro, Mexico*, M.O. Vazquez-Lepe,* Universidad de Guadalajara, Mexico*, F. Espinosa-Magaña*, CIMAV-Unidad Chihuahua, Mexico

Within the transition metal oxides, Fe oxides are among the most technologically relevant. Surfaces analysis through techniques such as X-ray photoelectron spectroscopy (XPS) plays a crucial role in the development of new applications. Despite that a considerable effort has been made on Fe oxides with XPS, many questions are still unanswered mainly due to the lack of a simple and standardized method to adequately model the spectrum of the Fe 2*p* core level. Complex characteristics such as a steeply background, shake-up satellites, and an asymmetrical line-shape, have been the principal obstacle to obtain accurate areas for proper quantification. In this work, this problem has been confronted by employing the SVSC background [1] and the double Lorentzian line shape [2]. The latter has many advantages over the traditionally employed Doniach-Sunjic line shape, since it is integrable and, then, suitable for quantitative studies.

With this combination of methods it has been possible to closely model the entire Fe 2*p* spectra (including both the 3/2 and 1/2 branches), which implied accounting for the shake-up satellite already known and the inclusion of a second satellite rarely reported in the literature. A proper determination of areas for accurate quantification of composition and thickness has been achieved taking into account this second satellite located around 725 eV (binding energy), hidden under the 1/2 branch of the main oxide peak. The inclusion of this second signal, together with the already known satellite, improves notably the quantitative analysis of the Fe oxides spectra. The position of the satellites shows a clear dependence on the oxide thickness. Thickness assessment has been confirmed with high-resolution transmission electron microscopy.

[1] A. Herrera-Gomez, M. Bravo-Sanchez, O. Ceballos-Sanchez, and M.O. Vazquez-Lepe. Journal of Electron Spectroscopy and Related Phenomena (in press) DOI 10.1002/sia.5453.

[2] A. Herrera-Gomez. "A double Lorentzian shape for asymmetric photoelectron peaks." Internal Report. Cinvestav-Querétaro.(2011). http://www.qro.cinvestav.mx/~aherrera/reportesInternos/doubleLorentzian.pdf

Biomaterial Interfaces
Room: 317 - Session BI+AS-MoM

Biomolecules & Biomaterials Interfaces
Moderator: Ilya Reviakine, CIC biomaGUNE

8:40am **BI+AS-MoM2 Deposition of Porous Polyparylene Layers with Even Thickness in Narrow Tubes**, ***Gerhard Franz**, H. Heidari*, Munich University of Applied Sciences, Germany

To coat a thin hollow tube with an equally thick layer along the whole length, is one of the most challenging issues of surface refinement. Even for long mean free paths and large diffusion lengths, a drop in thickness is common, which is simply caused by the abstraction of deposited molecules, which cannot walk randomly any longer. To overcome these inherent spatial inhomogeneities, we made use of the mechanism of the temperature-dependent surface polymerization, which is manifested in the occurence of a "ceiling temperature". Negatively turned, no deposition is possible beyond this temperature. Positively spoken, the spatially inhomogeneous deposition rate along a tube can be equalized with a counteracting temperature gradient. Experimentally, a configuration with four furnaces in line has been constructed which allows the inner wall of a tube 12" in length and 1/8" in inner diameter to be coated with a layer of even thickness. The most prominent application is the partial protection of thin silver layers which are deposited on the inner walls of catheters of polyurethane or polysilicone not as a contiguous film but with a zebra-stripe design applying a patent-pending procedure [1]. These silver rings act as antibacterial means to combat infections and induced incrustations in the urological area. To prolong the lifetime of the silver depot, it has to be protected with a porous human compatible top layer. We chose FDA approved polyparylene with thicknesses between 100 and 400 nm to ensure a long-term antibacterial activity, which should be kept above threshold level by a safety factor of 2 [2,3]. First results for the CVD of polyparylene are presented and are discussed and modeled with COMSOL in terms of diffusion laws with an abstraction reaction of 1st order. After having shown the antibacterial effect for a static case [4], here a dynamic trial is presented to simulate the antibacterial activity during flow of bacteria-containing urine in the ureters. [1] G. Franz, F. Schamberger, A. Kutschera, S. Seyedi, D. Jocham, German patent disclosure DE 102012023349.3, Nov. 29, 2012, [2] F. Schamberger, A. Ziegler, and G. Franz, J. Vac. Sci. Technol. B30, 01801 (2012) [3] G. Franz, F. Schamberger, J. Vac. Sci. Technol. A31, 061602 (2013) [4] H. Heidari, St. Sudhop, F. Schamberger, G. Franz, Biointerphases, accepted May 05, 2014

9:00am **BI+AS-MoM3 Deciphering the Scaling of Single Molecule Acid-Amine Interactions using Jarzynski's Equality**, *S. Raman, T. Utzig, T. Baimpos, B.R. Shrestha,* ***Markus Valtiner***, Max Planck Institut fur Eisenforschung GmbH, Germany

Unraveling the complexities of the macroscopic world based on molecular level details relies on understanding the scaling of single molecular interactions towards integral interactions, which are mediated through a large number of simultaneously interacting molecular bonds. Here we demonstrate how to decipher the scaling of acid-amine interactions from the single molecular level towards the macroscopic level through a synergistic experimental approach combining equilibrium Surface Forces Apparatus (SFA) experiments and non-equilibrium single molecule force spectroscopy (SM-AFM). Combining these two techniques is ideally suited for testing the largely praised Jarzynski's equality (JE), which relates the work performed under non-equilibrium conditions with the equilibrium free energy. Large-scale equilibrium force measurements using SFA scale linearly with the number density of acid-base bonds at an interface and we measure molecular acid-amine interaction energies of 10.9 ± 0.2 kT. AFM single molecule experiments reveal two distinct regimes. As expected, far from equilibrium the measured single molecule unbinding forces increase exponentially with the loading rate. A second quasi-equilibrium regime at loading rates close to and below the natural binding/unbinding rate of the acid-amine bond shows little loading rate dependence. Irrespective of how far from equilibrium AFM experiments are performed, the energy calculated using JE converges rapidly to 10.7 ± 1.1 kT. This is essentially equivalent to the value measured by the equilibrium measurements using SFA. Our results suggest that using Jarzynski's equality allows direct scaling of non-equilibrium single molecule interaction force measurements to scenarios where a large number of molecules are simultaneously interacting, giving rise to macroscopic equilibrated interaction energies. Taken together, the developed approach provides a strategy for molecular design of novel functional materials through predicting of large-scale properties such as adhesion or cell-substrate interactions based on single molecule or simulation experiments.

9:20am **BI+AS-MoM4 Fabrication of ssDNA Monolayers, Custom Designed ssDNA Arrays and Brush Patterns in Biorepulsive Templates by Promoted Exchange Reaction**, *M.N. Khan,* University of Heidelberg, Germany, *V. Tjong, A. Chilkoti,* Duke University, ***Michael Zharnikov***, University of Heidelberg, Germany

We present here a versatile approach to prepare mixed monolayers of thiolate-bound single stranded DNA (ssDNA) and oligo(ethylene glycol) substituted alkanethiols (OEG-AT) in a broad range of compositions as well as ssDNA/OEG-AT patterns of desired shape embedded into a biorepulsive background. The procedure involves two steps. First, a OEG-AT monolayer on a solid support is exposed to electrons or UV light in either homogeneous or lithographic fashion. Second, the promoted (by the irradiation in the first step) exchange reaction between the damaged OEG-AT species in the film and ssDNA substituents in solution occurs, resulting in formation of a ssDNA/OEG-AT monolayer or pattern. The composition of the mixed films or ssDNA/OEG-AT spots (lithography) can be precisely adjusted by electron or UV dose in almost entire composition range. The above procedure relies on commercially available compounds and is applicable to both thiol-terminated and symmetric and asymmetric disulfide-terminated ssDNA. The fabricated OEG-AT/ssDNA templates and patterns can be extended into the z-dimension by surface-initiated enzymatic polymerization of ssDNA, which results in the formation of highly ordered ssDNA brushes and allows topographically complex ssDNA brush patterns to be sculpted on the surface.

9:40am **BI+AS-MoM5 High Throughput BioMaterials Screening using Microarrays and High Information Content Imaging Methods**, *S. Boudjabi, D. Covelli, M. Keramane, E. Luckham,* ***John Brennan***, McMaster University, Canada **INVITED**

This presentation will highlight recent work in the area of high throughput screening of biologically modified surfaces for production of biosensors, protein and cell microarrays, and non-fouling surfaces. Using robotic material synthesis and assay systems and a combination of contact and noncontact microarray printing, we have produced several libraries of biomaterials with a wide range of chemical compositions based on acrylate, silicone and silica-based polymers. Using silica-based materials as an example, the presentation will show the workflow utilized to develop new bioactive polymer materials for generation of bioactive and stealth materials and coatings. This includes methods to produce several thousand materials very rapidly via printing, rapid imaging tools and assays for screening to identify "hits" that show a desired property (i.e., high bioactivity, low non-specific binding), and methods for detailed material analysis using a range of imaging methods based on fluorescence, XPS, MALDI-MS/MS, FTIR and SPR to fully characterize the properties of biologically active materials. Methods for mining and analyzing the large datasets produced using our in-house developed Biointerfaces Research Gateway will be described.

10:40am **BI+AS-MoM8 Osteocalcin Adsorption onto Calcium Phosphate and Silica Surfaces**, *L.A. Scudeller,* ***David Castner***, University of Washington

Osteocalcin (OC) is the most abundant, non-collagenous protein in bone and accounts for almost 2% of total protein in the human body. OC plays a role in the body's metabolic regulation and bone building, as well as being used as a biochemical marker for bone formation. However, its precise function is not known. OC is known to bind strongly to hydroxyapatite (HAP). This strong binding is likely the result of the γ-carboxylated glutamic acid residues (Gla) in OC interacting with Ca^{2+} ions on the HAP surface. OC has three helical units (α-1, α-2 and α-3) and the spacing of the 3 Gla residues in the α-1 unit match well the lattice spacing of the (001) HAP surface.

This study uses x-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) to investigate the adsorption of OC and decarboxylated (i.e., Gla converted back to Glu) OC (dOC) onto various calcium phosphate surfaces as well as silica surfaces. The XPS nitrogen signal is used to track the amount of adsorbed OC and dOC. The intensities of key ToF-SIMS amino acid fragments are used to assess changes in the structure of adsorbed OC and dOC.

The largest differences were observed between OC and dOC adsorbed onto the silica and HAP surfaces. Similar amounts (3-4 atomic % N) of OC and dOC were adsorbed onto the silica surface. Higher amounts adsorbed on the HAP surface (~5 atomic % N for dOC and ~8 atomic % N for OC). The ToF-SIMS data showed the intensity of the Cys amino acid fragment, normalized to intensity of all amino acid fragments, was significantly higher (~x10) when the proteins were adsorbed onto silica. Since in the native OC structure the cysteines are buried in the center of the 3 α-helices, this indicates both OC and dOC are more denatured on the silica surface. As OC and dOC denature upon adsorption to the silica surface the cysteines become more exposed and are more readily detected by ToF-SIMS. No significant differences were detected between OC and dOC adsorbed onto the silica surface, but small differences were observed between OC and dOC adsorbed onto the HAP surface. In the OC structure the α-3 helix is located above the α-1 and α-2 helices. Small differences in the ToF-SIMS intensities from amino acid fragments characteristic of each helical unit (Asn for α-1; His for α-2; and Phe for α-3) suggests either slight changes in the orientation or a slight uncovering of the α-1 and α-2 for adsorbed dOC.

XPS showed similar amounts of OC and dOC were absorbed onto amorphous HAP, crystalline HAP and octacalcium phosphate, but ToF-SIMS detected some small differences in the amino acid fragment intensities between adsorbed OC and dOC.

11:00am **BI+AS-MoM9 Reversible Activation of a pH-sensitive Cell Penetrating Peptides Attached to Gold Surfaces**, ***Joe Baio***, Oregon State University, *D. Schach,* University of Chicago, *M. Bonn, T. Weidner*, Max Planck Institute for Polymer Research, Germany

GALA peptides (WEAALAEALAEALAEHLAEALAEALEALAA) mimic pH-sensitive viral fusion proteins and are widely touted as a promising route to achieve site-specific delivery of therapeutic compounds. At basic pH, GALA assumes a random coil structure but when lowering the pH to acidic conditions the peptide transitions into an alpha helical structure. In this state, GALA has the ability to penetrate cell membranes and form pores. This mechanism is mainly driven by the change in overall charge of the glutamic acid side chains. One development of GALA mediated drug delivery is the immobilization of these peptides onto Au nanoparticles. Here we demonstrate, using a variety of spectroscopic techniques, that GALA can self-assemble into a protein monolayer on a gold film, linked to the surface via a single cysteine synthesized to the carbonyl terminus. Transmission IR vibrational spectroscopy demonstrates that the addition of this cysteine does not impede the pH transition between a helix and random coil structure in solution. Detailed characterization of the thiol-Au immobilization scheme by X-ray photoelectron spectroscopy illustrates that this single cysteine induced the formation of a well-ordered protein monolayer. To directly observe any pH triggered transition of this protein monolayer, sum frequency generation (SFG) vibrational spectra, at the amide I vibrational band, were collected at four different pH environments. A vibration mode at 1655 cm^{-1}, related to a helical structure, appears when this monolayer is immersed in a buffer at acidic conditions (pH 3 and 5) and then disappears under basic conditions (pH 9 and 12). While the surface immobilization clearly reduces the effective glutamic acid pK_a from a bulk solution value of 6 to 5.5, the covalently bound GALA-cysteine monolayer reliably retained the reversible, pH-driven helix-coil transition mechanism. Our findings establish that covalent attachment of GALA via cysteine linkers is a promising route for drug delivery applications and the design of 'smart' biological coatings.

11:20am **BI+AS-MoM10 Polydopamine Modification Using Small Molecule Thiols and Dithiols: Problems and Solutions for Creating Protein Resistant Coatings**, ***Marlon Walker***, *A. Vaish, D. Vanderah*, National Institute of Standards and Technology (NIST)

Polydopamine (PDA) is emerging as an increasingly useful bio-inspired coating for surface modification. Generated by a condensation reaction of dopamine in aqueous media under alkaline conditions, it can be readily deposited on almost any surface, forming thin films of controllable thicknesses. One useful attribute of a PDA coating is that it can be placed on and further modified to exhibit desired properties not possible with the underlying substrate. We present results of functionalizing PDA-coated surfaces on substrates such as silicon with oligo (ethylene oxide) thiols and dithiols for non-specific protein adsorption resistance.

11:40am **BI+AS-MoM11 A Process to Functionalize Polyaniline for Biotin-Avidin Biosensing**, ***Tiana Shaw***, *M.D. Williams*, Clark Atlanta University

Biotin-avidin technology is a widely explored interaction in bioscience. Biotin's affinity for the protein avidin, makes it ideal for protein and nucleic acid detection or purification methods. This strong interaction if often used in pretargeting strategies for cancer treatment. In most cases a probe molecule (antibody) is connected to a marker molecule (fluorophore or nanoparticle) through the biotin-avidin bridge. Biotinylated nanoparticles can play a role in improving this interaction and creating an electronic or optical detection method. Polyaniline is a polymer which can be easily functionalized to be specific for various biomolecules and has ideal sensor characteristics. In this study we will design a process to functionalize polyaniline with biotin to create a biotin-avidin biosensor. We began with 2-acetamidophenol which is a hydroxyl substituted aniline monomer. This monomer undergoes polymerization to yield 2-hydroxy polyaniline. The polymer's hydroxyl group was functionalized by Steglich esterification which refluxes a carboxylic acid with an alcohol. This esterification drives the reaction and dehydrates the products shifting the equilibrium towards the product. In this reaction DCC (dicyclohexylcarbodiimide) activates the carboxylic acid of biotin to further reaction and DMAP (4-dimethlyaminopyridine) acts as the acyl transfer catalyst. The biotinylated polyaniline derivative was characterized using FT-IR spectroscopy, ^1H NMR spectroscopy, UV-VIS spectroscopy, and Scanning Electron Microscopy. Florescence emission studies were also carried out with the avidin protein.

Materials Characterization in the Semiconductor Industry Focus Topic
Room: 313 - Session MC+AP+AS-MoM

Characterization of 3D Structures, 2D films and Interconnects

Moderator: Paul Ronsheim, CTO, PAR Technical Consulting, previously with IBM, Paul van der Heide, GLOBALFOUNDRIES, NY, USA

8:20am **MC+AP+AS-MoM1 Dopant/Carrier and Compositional Profiling for 3D-Structures and Confined Volumes.**, ***Wilfried Vandervorst***, *A. Kumar, J. Demeulemeester, A. Franquet, P. Eyben, J. Bogdanowicz, M. Mannarino, A. Kambham, U. Celano*, IMEC, KU Leuven Belgium **INVITED**

The introduction of three-dimensional devices (FinFets, TFETs and nanowires), has created as new metrology challenges the characterization of dopant /carrier and impurity distributions in 3D-devices and confined volumes. Beyond these dimensional challenges, the use of alternative materials such SiGe, Ge, GeSn alloys as well as III-V materials, adds to the metrology requirements. Recent evolution towards growth (and strain relaxation) mediated by the confined volume (for instance relying on aspect ratio trapping) calls for metrology suited for very small volumes and more atomic scale observations. Metrology in 3D-structures and confined volumes has demonstrated that the changing surface/volume ratios in confined devices versus blanket films lead to phenomena (dopant deactivation, enhanced diffusion,..) which cannot be observed in blanket experiments. Hence more emphasis should be placed on the analysis of device and structures with relevant dimensions relative to the exploration of blanket experiments.

Atomprobe tomography is able to provide composition analysis within very small volumes (a few nm3) with high sensitivity and accuracy and excellent spatial resolution. Hence this enables to observe dopant atom migration in 3D-devices, and through some data mining analysis, even cluster formation as precursor to strain relaxation such as seen in metastable alloys like GeSn. Field Ion Microscopy, a complement to APT, can be used to image impurity atoms clustered around defects within the crystal. Routine application of APT is still hampered by localization problems, reconstruction artifacts due to inhomogeneous evaporation, local magnification effects, sensitivity due to the limited statistics, laser-tip interaction phenomena, etc.

Although scanning spreading resistance microscopy is inherently 2D, analysis of 3D-devices (FinFet, ReRam, Sonos..) is possible by novel approaches such as SPM scalping. The introduction of novel modes such as soft retrace, FFT-SSRM has led of improved resolution and eliminates series resistances resulting from the current confinement in these narrow devices, decoupling the actual "spreading resistance" from the total resistance. Finally SSRM-carrier distribution have been coupled to device simulators leading to an accurate prediction of device performance.

In addition to APT we also present here the concept of "self focusing SIMS" whereby we demonstrate that it is possible to determine, for instance, the SiGe(III-V) composition in trenches as small as 20 nm without having an ion beam with nm-resolution. This represents a significant step forward in terms of production control and statistical relevance.

9:00am **MC+AP+AS-MoM3 Characterization of the Periodicity (Pitch) and Stress of Transistor Fin Structures using X-Ray Diffraction Reciprocal Space Mapping**, ***Alain Diebold***, *M. Medikonda*, SUNY College of Nanoscale Science and Engineering, *M. Wormington*, Jordan Valley Semiconductors Inc

Cleanroom compatible, high resolution X-Ray diffraction systems are now capable of measuring the average pitch and critical dimensions of ordered arrays of fins and the stress state of high mobility layers at the top of the fins. Reciprocal Space Mapping (RSM) characterizes both the main Bragg diffraction peak and the satellite peaks associated with the fin periodicity. The periodicity of the fin arrays has decreased to the point where the fin array adds satellite diffraction peaks to the main Bragg diffraction peak from the semiconductor. The pitch can be calculated from the angular spacing of the satellite peaks. State of the art lithographic processing using the spacer patterning process often results in a different spacing between every other fin. This is known as pitch walking. Pitch walking is very difficult to observed, even using TEM cross-sectional images. The stress state of the high mobility epilayers such as $Si_{1-x}Ge_x$ on Si fins can also be characterized using RSMs. In addition, some of the higher order satellite peaks will split when the fins have a near rectangular shape. This presentation compares the capability of cleanroom and synchrotron based

XRD systems for reciprocal space mapping of Si and $Si_{1-x}Ge_x$ / Si transistor fins arrays.[1]

[1] Measurement of Periodicity and Strain in Arrays of Single Crystal Silicon and Pseudomorphic $Si_{1-x}Ge_x$/Si Fin Structures using X-ray Reciprocal Space Maps, M. Medikonda, G. Muthinti, J. Fronheiser, V. Kamineni, M. Wormington, K. Matney, T. Adam, E. Karapetrovaand A.C. Diebold, J. Vac. Sci. Technol**.** **B32**, (2014), 021804.

9:20am **MC+AP+AS-MoM4 MBE Grading Techniques for the Growth of InAsSb Films with Inherent Properties Unaffected by Strain**, ***Wendy Sarney***, *S.P. Svensson,* US Army Research Laboratory, *Y. Lin, D. Wang, L. Shterengas, D. Donetsky, G. Belenky*, Stony Brook University

By using compositionally graded buffer layers, InAsSb can be grown by molecular beam epitaxy with its inherent lattice properties across the entire composition range. This direct bandgap, III-V alloy is of great interest for infrared detector applications, as it can cover both the mid (3-5 µm) and long wavelength (8-12 µm) bands. The direct bandgap provides the high quantum efficiency that allows it to directly compete with HgCdTe but at potentially much reduced fabrication costs. InAsSb was sidelined for decades, because conventional wisdom indicated its bandgap bowing parameter would not allow it to reach the needed 10-12 µm benchmark. The material was further maligned because it was thought to exhibit CuPt ordering, which affects the bandgap. By revisiting the growth techniques we have determined that the bandgap bowing parameter of InAsSb is more than sufficient for LWIR applications and it can be grown free of ordering, provided that the material is grown with its inherent, undistorted lattice constant.

As there is no perfect substrate available for the InAsSb compositions of interest (typically containing ~40-50% Sb), we grow the films on compositionally graded buffer layers on GaSb substrates. The buffer layers consist of AlGaInSb, GaInSb, or InAsSb grades based on the theories described by J. Tersoff.[1] In this paper we provide experimental verification of Tersoff's theories applied to ternary and quaternary grades, and for both tensile and compressive grades. Furthermore, the specific parameters calculated by Tersoff, such as the boundary for the dislocation-free region (Zc) is exactly verified by transmission electron microscopy (TEM).

Reciprocal space maps show that the InAsSb layers grown on compositional graded buffer layers have their native lattice constant. The films are free from strain-relieving dislocations within the field of view allowed by TEM. Furthermore, we see no evidence of group V ordering for films grown in this manner. Although ordering is known to further reduce the bandgap, it is a difficult property to control, and it would be very undesirable to rely on it to induce the needed longer wavelengths. We have observed that a finite amount of residual strain that is small enough not to cause dislocation formation can induce CuPt ordering, but this can be completely avoided by using appropriate grading techniques. We also see no evidence of phase segregation or miscibility gaps.

Photoluminescence wavelengths have been measured for numerous InAsSb films, with a maximum wavelength to date of 12.4 µm. This may be the ideal material for direct bandgap infrared device applications.

J. Tersoff, Appl. Phys. Lett. 62, 693 (1993);

9:40am **MC+AP+AS-MoM5 Quantitative 3-D Imaging of Filaments in Hybrid Resistive Memory Devices by Combined XPS and ToF-SIMS Spectroscopies**, *Y. Busby,* ***Jean-Jacques Pireaux***, University of Namur, Belgium

Resistive switching has been observed in a multitude of inorganic (oxides, chalcogenides...) and hybrid (organic or polymers plus metal nanoparticles) thin films simply sandwiched between two metal electrodes. Organic memory devices are particularly promising candidates for developing large scale, high density, cost efficient, non-volatile resistive memories. Their switching mechanism has been for a long time suggested to depend on the formation/rupture of localized conducting paths (filaments). Using electrical characterization by impedance spectroscopy, filament formation has been experimentally demonstrated to be the dominant switching mechanism in many organic memories, only very recently (2014). Otherwise, despite of very dedicated efforts, few experimental techniques have so far succeeded in characterizing and providing information on filament(s).

The present work combines for the first time High Resolution X-Ray induced Photoelectron Spectroscopy (for its quantitative information capability) and Time-of-Flight Secondary Ion Mass Spectrometry (for its very high atomic sensitivity and 3D imaging capabilities) to quantitatively study both lateral and in depth elements distribution in a complete and operative organic memory device: what happens to be top electrode metal diffusion and filament formation is evidenced and quantitatively evaluated in memory devices which are based on a highly insulating and *cross-linked polystyrene layer*, processed by plasma polymerization, sandwiched between silver and indium tin oxide electrodes. Depth profiles evidence the metal diffusion in pristine and electrically addressed memory elements through the whole organic layer where the silver concentration can reach value as high as 5.10^{19} at/cm^3. Filament formation is shown to be initiated during the top electrode evaporation, and is then successively enhanced by field induced diffusion during the electrical addressing. The 3-D ToF-SIMS images evidenced the formation of metallic paths extending through the entire device depth, electrically bridging the two electrodes when the element is in its low resistance state. Filaments with different characteristics have also been studied in organic memories based on a semiconducting polymer (Polyera N1400 ActiveInk) or on semiconducting small molecules (Tris-(8-hydroxyquinoline)aluminum, AlQ_3). It appears therefore that metallic filaments are indeed at the origin of switching in organic memory devices.

10:00am **MC+AP+AS-MoM6 High Throughput Electron Diffraction-Based Metrology of Nanocrystalline Materials**, *X. Liu,* Carnegie Mellon University, *D. Choi,* Korea Railroad Research Institute, Republic of Korea, *N.T. Nuhfer,* Carnegie Mellon University, *D.L. Yates, T. Sun,* University of Central Florida, *G.S. Rohrer,* Carnegie Mellon University, *K.R. Coffey,* University of Central Florida, ***Katayun Barmak***, Columbia University

The resistivity of Cu, the current interconnect material of choice, increases dramatically as the conductor's dimensions decrease towards and below the mean free path of electrons (39 nm at the room temperature). Two scattering mechanisms that contribute to this resistivity size effect are surface scattering, evidenced by thickness dependence of resistivity, and grain boundary scattering, evidenced by grain size dependence of resistivity. Quantification of microstructural parameters, such as grain size, at the scale of the resistivity size effect necessitates the use of transmission electron microscopy (TEM). In this work, an electron diffraction-based orientation mapping system installed on the TEM is used to characterize not only nanometric Cu films, but also new materials, W, Ni, Ru and Co, that are potential candidates to replace Cu as the next-generation interconnect material. In this characterization technique, spot diffraction patterns are collected as the nano-sized beam scans the area of interest. The crystallographic orientation of each scanned pixel is determined by cross-correlation with pre-calculated diffraction patterns (termed, templates). Precession is used to reduce the dynamical scattering effects, increasing the reliability of the orientation mapping. The raw orientation data is then processed to yield the microstructural data via a well-defined procedure developed to parallel that used to process electron backscatter orientation data taken in scanning electron microscopes. This characterization yields full range of microstructural parameters including grain size, grain size distribution, orientation distribution, misorientation distribution, grain boundary and interface character and plane distribution that are extracted from the crystal orientation maps in a nearly fully-automated manner. These microstructural parameters, along with sample thicknesses, are used to evaluate the validity of the semiclassical resistivity size models for Cu and the new materials, and, where applicable, to determine the relative contributions of surface and grain boundary scattering to the resistivity increase.

10:40am **MC+AP+AS-MoM8 LEIS Characterization of the Outer Surface, Ultra-Thin Layers and Contacts**, ***Hidde Brongersma***, ION-TOF / Tascon / Calipso, Netherlands, *P. Bruener, T. Grehl,* ION-TOF GmbH, Germany, *H.R.J. ter Veen*, Tascon GmbH, Germany **INVITED**

Modern day technologies are increasingly based on high performance nanomaterials and novel preparation techniques for such materials are developed at a rapid pace. Advances in nanoscience and nanotechnology heavily rely on the availability of analytic techniques that can validate and support new nanomaterials synthesis procedures. With the introducing of the Qtac^{100}, a new high-sensitivity Low Energy Ion Scattering (HS-LEIS) instrument, one can quantitatively analyze the atomic composition of the surface of a wide range of materials with an unparalleled surface sensitivity.

The outermost atoms of a surface largely control processes such as growth, nucleation, poisoning, adhesion and electron emission. While analytic tools (such as XPS) probe an average of many atomic layers, LEIS can selectively analyze the outer atoms. In addition, non-destructive in-depth information, with high depth resolution, is obtained for the heavier elements (0 - 10 nm). HS-LEIS is just as well suited for the *quantitative analysis* of amorphous, insulating and extremely rough surfaces as for flat single crystals. Since HS-LEIS is a fast analysis technique, it can be used to follow diffusion processes in-situ.

The focus will be on applications where valuable information has been obtained that is impossible (or very difficult) to obtain with other analytical techniques. The unique possibilities will be illustrated with state-of-the-art applications for: ALD growth of ultra-thin layers, surface modification, interface diffusion, core/shell nanoparticles, graphene, self-assembled monolayers for sensors.

The findings will be compared and contrasted to those obtained by other analytic techniques such as XPS, Auger, SIMS, RBS and conventional LEIS.

11:20am **MC+AP+AS-MoM10 Backside versus Frontside Characterization of High-k/Metal Gate Stacks for CMOS sub-14 nm Technological Nodes**, ***Eugenie Martinez,*** CEA, LETI, MINATEC Campus, France*, B. Saidi, P. Caubet, F. Piallat,* STMicroelectronics, France*, H. Kim,* CEA, LETI, MINATEC Campus, France*, S. Schamm-Chardon,* CEMES-CNRS, France*, R. Gassilloud*, CEA, LETI, MINATEC Campus, France

Down-scaling of CMOS transistors beyond the 14 nm technological node requires the implementation of new architectures and materials. The gate last integration scheme is a promising solution to better control the threshold voltage of future MOSFETs, because of its low thermal budget [1]. Advanced characterization methods are needed to gain information about the chemical composition of such structures. The analysis of thin layers and interfaces buried under a thick metal electrode is particularly challenging. An effective approach based on backside sample preparation is proposed here.

To tune the work-function toward nMOS values, the technology currently investigated is based on HfO_2 for the dielectric and a thin TiN layer capped by a TiAl alloy for the gate [2]. For a better understanding of aluminium and other elements redistributions after a 400°C annealing, a specific methodology has been developed based on the removal of the Si substrate. It allows to achieve XPS and Auger analyses from the backside of the sample [3].

In particular, Auger depth profiling performed on HfO_2/TiN/TiAl/TiN/W gate stacks at low energy (500 eV Ar^+) brought the following main conclusions: a) no Al diffusion toward the HfO_2/TiN interface, b) nitrogen out diffusion in the upper TiAl film, c) significant oxygen scavenging. By comparison, these results evidenced that Auger frontside analyses suffer from sputter-induced artifacts.

In a further study, to understand the behavior of nitrogen out diffusion in the TiAl layer, we deposited $TiAlN_x$ thin films with various nitrogen flows by reactive sputtering deposition and performed backside XPS analyses. At low/medium nitrogen flows, which correspond to the $TiAlN_x$ film after TiN/TiAl bilayer anneal, the N1s core level spectra obviously shows that N is mainly bonded to Al rather than Ti. Results are compared with frontside XPS performed with a thinner TiN upper layer. The backside approach is shown to be more representative of the technological stack, in particular with respect to the TiN oxidation.

Measurements were carried out at the NanoCharacterization Platform (PFNC) of MINATEC.

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[2] A. Veloso et al.., Symposium on VLSI Technology, Digest of Technical Papers (2011).

[3] M. Py et al., AIP conference proceedings 1395, 171 (2011).

11:40am **MC+AP+AS-MoM11 Charge Storage Properties of Al/$(1-x)BaTiO_{3-x}Ba(Cu_{1/3}Nb_{2/3})O_3$ (x = 0.025) (BTBCN)/HfO_2/p-Si Metal/Ferroelectric/Insulator/Semiconductor Devices***, **Souvik Kundu**, M. Clavel, D. Maurya, M. Hudait, S. Priya*, Virginia Tech

Metal-ferroelectric-insulator-semiconductor (MFIS) devices with pulsed laser deposited 300 nm $(1-x)BaTiO_{3-x}Ba(Cu_{1/3}Nb_{2/3})O_3$ (x = 0.025) (BTBCN) ferroelectric film and atomic layer deposited 10 nm HfO_2 insulating layer on silicon semiconductor substrate were developed for next generation ferroelectric non-volatile memory applications. For the first time, the structural, interfacial, and electrical properties of these Al/BTBCN/HfO_2/p-Si MFIS devices were studied, and the role of BTBCN as charge storing elements was also established. The X-ray diffraction and transmission electron micrograph with selected area diffraction pattern clearly demonstrate the single crystallization of BTBCN ferroelectric films. It was found that insertion of 10 nm HfO_2 in-between BTBCN and Si improves the interfacial properties and also prevents the interdiffusion of semiconductor into the ferroelectric layer. The optical bandgap of BTBCN was found to be 4.38 eV using transmission spectrum analysis. The MFIS structure showed capacitance-voltage hysteresis loops due to the ferroelectric polarization of BTBCN and the maximum memory window was found to be 1.65 V when the sweeping voltage was ±10 V. However, no memory window was found in metal-insulator-semiconductor devices, i.e., when there is no BTBCN layer in between metal and insulating layer. The leakage current of these devices was found to be 7×10^{-9} A/cm^2 at an applied voltage of -1 V. The wide memory window and superior retention properties were achieved due to the presence of BTBCN. The electronic band diagrams of these MFIS devices during program and erase operations were proposed.

Keywords: BTBCN; MFIS; Memory window; Leakage current; Band-diagram

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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[4] T. Giamarchi, *Quantum Physics in One Dimension* (Oxford University Press, New York, 2004).

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 $(2.3 \pm 0.5) \text{ X } 10^{-3}$. 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 $(5.5 \pm 0.6) \text{ X } 10^{-3}$ 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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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*-$PtCl_2(CO)_2$.

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.

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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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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.

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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 $4f$ 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 $4f$ 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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Biomaterial Interfaces
Room: 317 - Session BI+AS+NS-MoA

Bio/Nano Interfaces
Moderator: Patrick Koelsch, University of Washington

2:00pm **BI+AS+NS-MoA1 Controlling Bio/Nano Interface Response using Metal Oxide Atomic Layer Deposition: Zinc Oxide ALD Modifies how Human Lung Fibroblasts respond *In Vitro* to Multiwall Carbon Nanotubes**, ***Erinn Dandley***, *A. Taylor, G.N. Parsons, J. Bonner*, North Carolina State University

Carbon nanotubes have been reported to cause pulmonary fibrosis in mice after inhalation exposure. When inhaled, multiwall carbon nanotubes (MWCNTs) activate macrophage inflammasomes and interleukin (IL)-1β release, key cellular components of the innate immune response. Macrophages are the first line of defense that engulf and remove inhaled MWCNTs from the lungs. Macrophages are also a source of secreted osteopontin (OPN), which promotes tissue matrix remodeling and fibrosis. These responses may be triggered by the unique aspect ratio, aggregation or surface chemistry of MWCNTs. In previous studies, we explored atomic layer deposition (ALD) as a means to modify the surface functionality of MWCNTs and studied how the surface coating affected the toxic response of THP-1 cells, a widely used human monocyte/macrophage cell line, and primary peripheral blood monocytes (PBMCs) obtained from normal human donors. Compared to uncoated MWCNTs, we found that nanotubes with Al_2O_3 nanocoatings showed enhanced IL-1β secretion and decreased OPN production in THP-1 cells and PBMCs, indicating that the coating enhances the innate immune response and decreases pro-fibrotic activity.

In this study we examined the effect of ALD ZnO coatings on the fibrogenic response in human lung fibroblast (HLFs) using mRNA expression and secretion of transforming growth factor (TGF)-b 1 and CXCL10, mediators that promote and deter fibrosis respectively. We find that the ALD ZnO layer thickness can be controlled down to ~5nm, and the thickness scaled directly with the number of ALD cycles, as observed by TEM. Thicker coatings inhibited MWCNT aggregation, and sonication allowed us to induce fiber fragmentation. In this way the ALD coating allowed us to independently adjust surface termination, fiber aggregation, and fiber aspect ratio, providing us a unique tool to examine how each of these factors influences cellular response. Initial results show that the ZnO coating significantly increased TGF-β1 mRNA expression and stimulated a larger pro-fibrogenic response in HLFs compared to uncoated MWCNTs. Control experiments using ZnO nanoparticles also showed potent induction of TGF-β1 mRNA in HLFs. Also, the response tends to correlate with extent of dispersion, and is nearly independent of MWCNT aspect ratio. These experiments show that nanoscale surface functionalization of nanoscale materials may help us gain better understanding of the mechanisms associated with toxicology of nanomaterials, and expand knowledge of biological response at nano/bio interfaces.

2:20pm **BI+AS+NS-MoA2 Mechanically Optimized Fe (III) Doped Silica Nanoshells as a Contrast Agent for Ultrasound Imaging and HIFU Therapy**, ***James Wang***, *A. Liberman, R. Viveros, C. Barback, S.L. Blair, Z. Wu, R. Mattrey, W. Trogler, A.C. Kummel*, University of California at San Diego

Ultrasound (US) is a common medical imaging modality due to its flexibility, low-cost and therapeutic potential. 500 nm silica nanoshells were synthesized as a contrast agent to improve US imaging signal for better diagnostic performance. Iron (III) was included into the silica network to enhance the biodegradability of the silica nanoshells. Previously, ferric iron was shown to facilitate silica nanoshell biodegradation due to its strong binding affinity with serum transferrin proteins. The removal of iron from the silica network by serum proteins fragments the nanoshells enabling effective biodegradation for *in vivo* applications. The silica nanoshells are filled with perfluorocarbon (PFC) vapor which expands and shatters the nanoshells during US irradiation. A mechanically weaker silica nanoshell increases US signal at lower power. A range of alkoxysilanes with selected R-groups such as long chain hydrocarbons, fluorinated carbon chains, fluorinated phenyl groups and vinyl groups were employed along with tetramethyl orthosilicate and iron (III) ethoxide in a modified sol-gel synthesis to create structural defects that alter the mechanical properties of the nanoshells. Monodispersed 500 nm polystyrene beads were used as a soft template during the reaction. The silica nanoparticles were calcined at 550 C to remove the polystyrene core and form hollow nanoshells. SEM and TEM showed that 500 nm silica nanoshells with different microstructures were synthesized incorporating alkoxysilanes with different R-groups. Formulations with higher concentrations of alkoxysilanes with large R-groups such as long chain hydrocarbons resulted in stronger *in vitro* contrast enhanced ultrasound (CEUS) signals due to the increase of structural voids that resulted in weaker shell strength. CEUS experiments demonstrated that mechanically weaker silica nanoshells exhibited longer signal life time and required a lower mechanical index (MI) for imaging. The high intensity focused ultrasound (HIFU) properties of the modified silica nanoshells were tested for potential therapeutic applications. Mechanically weaker silica nanoshells were shown *in vitro* to require a lower HIFU power to fracture which is consistent with safer HIFU therapy. By synthesizing strength tunable silica nanoshells as US contrast agents, it is possible to improve diagnostic US imaging performance in order to detect smaller tissue structures or early stage tumors. Additionally, mechanically weaker silica nanoshells may also increase the efficiency of HIFU enabling HIFU at lower US power and/or higher speed.

2:40pm **BI+AS+NS-MoA3 Synthesis, Functionalization, and Biological Imaging with Quantum Dots**, ***Preston Snee***, University of Illinois at Chicago **INVITED**

Semiconductor quantum dots (QDs, or nanocrystals), are very bright chromophores that possess unlimited potentials in alternative energy generation and for biological sensing and imaging applications. Our group has made advances in the synthesis QDs to produce 100% efficient emitters; furthermore, we can dope the semiconductor with guest ions to alter the bandgap. We recently invented a method to dope each quantum dot with an exact number of guest ions, a feat that was previously considered impossible. As very bright fluorophores, quantum dots are ideal for biological imaging and sensing. Our first contribution in this regard was to develop methods of chemical and biological functionalization of water-soluble quantum dots as many existing methods either quenched the QDs or had very low reaction yields. We have circumvented these problems by synthesizing polymers which serve as QD functionalization reagents; the polymer – QD activated intermediate has increased stability and allows us to conjugate chemical and biological vectors to the nanocrystals with ~100% reaction yields. We use these methods to functionalize QDs with organic fluorophores that can report on the local chemical and biological environment. We have synthesized several ratiometric, or “self-calibrating” sensors, for pH, toxic metals, DNA, and proteins. In our recent work on protein sensing, we have developed an all optical method for sensing un-labeled proteins with a better detection limit than any currently existing technology. We have also circumvented the well-known problem of cytocellular delivery of quantum dots into live, adherent cells.

3:40pm **BI+AS+NS-MoA6 Easynanofab: Fast, Simple, Combinatorial Routes to Reusable Plasmonically Active Gold Nanostructures Over Macroscopic Areas**, *A. Tsargorodska, O. El Zubir,* ***Graham Leggett***, University of Sheffield, UK

Plasmonic effects associated with gold nanocrystals have attracted widespread interest for the interrogation of biological molecules. Existing approaches to fabrication of plasmonic nanostructures fall into two categories: high precision methods such as electron beam lithography that rely on complex, specialised infrastructure; and simple, low-cost methods such as colloidal lithography that offer limited capacity. Here, we describe a fast, simple method for the fabrication of re-usable, robust gold nanostructures over macroscopic (cm^2) areas that provides enormous scope to control nanostructure morphology and dimensions, and which also uses only simple apparatus and requires no access to a clean-room. We have assembled a combinatorial library of over 200 different samples consisting of highly crystalline gold nanostructures that exhibit varying morphologies, dimensions and periodicities but yield intense plasmon bands. These structures enable the rapid identification of optimum substrates for the detection and analysis of biological targets, and provide a platform for exploring the relationship between particle morphology and optical properties. Self-assembled monolayers (SAMs) of alkylthiolates on chromium-primed polycrystalline gold films are patterned using a Lloyd’s mirror interferometer and etched using mercaptoethylamine in ethanol in a rapid process. The use of a Cr adhesion layer facilitates the cleaning of specimens by immersion in piranha solution, enabling their repeated re-use without significant change in their absorbance spectra over two years. Annealing yields structures with a uniformly high degree of crystallinity that exhibit strong plasmon bands. Because of the ease with which nanoparticle morphology may be controlled using interferometric lithography (IL), it provides a convenient means to investigate the correlation between structural parameters (particle dimensions, spacing) and optical responses. The shift in the position of the plasmon band after site-specific attachment of histidine-tagged green fluorescent protein (His-GFP) and after adsorption of chlorophyll and bacteriochlorophyll was measured for a range of nanostructured films, enabling the rapid identification of structures that yielded the largest shifts. Strong resonant coupling was observed when light-harvesting membrane protein complexes from plants and bacteria were coupled to gold nanostructure arrays, yielding absorbance spectra that were very different from those of the clean gold nanostructures. This approach offers a simple route to the production of durable, reusable, macroscopic arrays of gold nanostructures with precisely controllable morphologies.

4:00pm **BI+AS+NS-MoA7 Impacts of Nanoparticle Synthesis Route, Structure and Serum Proteins on the Dispersion and Dissolution of Ag Nanoparticles in Biological Media**, *P. Munusamy, J.N. Smith, C. Liu, C.-M. Wang,* Pacific Northwest National Laboratory, *S. Chen,* Imperial College London, UK, *M.H. Engelhard,* Pacific Northwest National Laboratory, *A.E. Porter, M.P. Ryan,* Imperial College London, UK, ***Donald Baer***, Pacific Northwest National Laboratory

The wide-spread use of silver nanoparticles in consumer products raises questions of environmental impact and toxicity. Because both silver particles, and silver ions formed by particle dissolution, may impact biological systems, it is important to understand the characteristics of silver nanoparticles as they are made and their stability and dissolution in the medium relevant to environmental and toxicological studies. Silver nanoparticles produced by different synthesis routes can have significantly varying physical and chemical characteristics. In this talk we will summarize the characterization and dissolution stability of three types of silver nanoparticles (20 nm particles synthesized with and without gold core (~7 nm) and 110 nm particles with gold core) in cell culture media with serum proteins: FBS10%/RPMI, the culture media used at Pacific Northwest National Laboratory for *in-vitro* toxicity studies. These nanoparticles were synthesized and prepared for biological study in aqueous solution. They were examined *in situ* using dynamic light scattering, zeta potential measurements and optical adsorption and *ex situ* with x-ray photoelectron spectroscopy and transmission electron microscopy. For the dissolution studies, concentrations of particles examined were varied from 1 µg/ml to 50 µg/ml, consistent with the range of concentrations typically used during *in-vitro* studies. Silver particles with gold cores had smaller crystallite size and higher apparent solubility than three different batches of pure ~ 20 nm silver particles. A simple dissolution model was found to describe the time variation of particle size and amount of dissolved silver for particle loadings above 9 µg/ml. The effective solubility product obtained from fitting the data was higher for the 20 nm particles with the gold core in comparison to the pure silver or 110 nm particles. The dissolution of silver nanoparticles was also found to be enhanced by presence of serum proteins contained in fetal bovine serum (FBS). In addition, the protocol of dispersion in cell culture medium was found to influence particle agglomeration and the rate of dissolution. In these measurements focusing on a 24 hour time point, we found that the structure of the silver nanoparticles can have a significant impact on the concentration of dissolved silver in media and thus the dosimetry to which cells would be exposed during in vitro studies.

This work has been supported by the NIEHS under Center grant U19 ES019544. Portions of this work were performed using EMSL, a national scientific user facility sponsored by the US Department of Energy, Biological and Environmental Research and located at PNNL.

4:20pm **BI+AS+NS-MoA8 Analysis of Protein Coated Nanoparticles by X-ray Photoelectron Spectroscopy and Solution-Based Particle Size Techniques**, *C. Minelli,* ***Natalie Belsey***, *A.G. Shard,* National Physical Laboratory, UK

The attachment of proteins to nanoparticles’ surface is of increasing interest in medicine for applications such as drug delivery and diagnostics. The unintentional acquisition of a protein corona from biological media is also important in determining the performance and potential toxicity of such particles. Understanding and refinement of the performance of nanoparticles of use in medical applications require accurate and quantitative characterisation of their protein interface. Our efforts are focussed upon developing measurement techniques to enable useful characterisation of this interface. In this study, three biomolecules of a range of sizes, shapes and mechanism of interaction with gold surfaces, i.e. 16 AA peptide, BSA and IgG, were adsorbed to gold nanoparticles (10, 20, 40, 60 and 80 nm) and the shell thickness was measured in solution using dynamic light scattering (DLS) and differential centrifuge sedimentation (DCS). UV-visible spectrophotometry was used to monitor localised surface plasmon resonance (LSPR) shifts of the nanoparticles due to the acquisition of the protein shell. Combination of this information with thickness measurements allowed for an estimation of the protein shell refractive index and average number of biomolecules at the nanoparticle surface. X-ray photoelectron spectroscopy (XPS) analysis of the same nanoparticles deposited on a PTFE substrate enabled determination of the nanoparticle shell chemical composition and dehydrated thickness, from which the number of molecules at the nanoparticle surface was also estimated. Parallel characterisation of the nanoparticles in their colloidal form and in vacuum provided consistent results and the combination of the techniques revealed farther insight into molecular adsorption at nanoparticles’ interfaces. The complementarity of the approaches also allowed for validation of the methods, which is important for their application to a wide range of nanoparticle types. For example, DLS and LSPR analysis are not suitable for dealing with aggregated samples, but XPS is, while XPS measurements of organic nanoparticles are challenging and liquid based techniques may be preferred.

4:40pm **BI+AS+NS-MoA9 Development of Nanofibrous Meshes as Smart Dressings for Chronic Wound Care**, ***Martina Abrigo***, *P. Kingshott, S.L. McArthur*, Swinburne University of Technology, Australia

Diabetic, pressure, venous and arterial ulcers are a large social, economic and healthcare burden. These chronic non-healing wounds show delayed and incomplete healing processes exposing patients to high risk of infection. The design of wound dressings that combine the necessary morphological and physical requirements for wound healing with the value-added capability to address optimal cell responses and impair bacterial proliferation represents a major challenge in chronic wound care. Polymeric nanofibrous meshes fabricated through the electrospinning process are promising candidates as wound dressings due to their high surface area, micro-porosity and non-woven structure. In this study, the parameters of the electrospinning process (such as spinning rate and electric field intensity) were optimized to fabricate nanofibrous membrane in Polystyrene (M.W. 250.000). The morphological properties of the electrospun meshes were analysed by bright microscopy, three-dimensional optical profiler, Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). Electrospun materials have been used as scaffolds for tissue engineering for a number of years, but there is surprisingly little literature on the interactions of fibres with bacteria. In order to understand microbial infiltration and control in wound dressings, a number of microbiological assays (MTT, MTS and live/dead) were completed using *E. Coli*, *P. Aeruginosa*, *S. Aureus* in an effort to understand how the morphological and structural properties of the electrospun meshes influence bacterial attachment, proliferation and growth.

5:00pm **BI+AS+NS-MoA10 Electrophoretic Stretching of Tethered DNA in Nanoslits**, ***Jia-Wei Yeh***, *K. Szeto, H.G. Craighead*, Cornell University

We have investigated the field-extension of tethered DNA in nanoslits with slit heights ranging from 30 to 130 nm, and performed an analysis from an approximated modified worm-like chain (mWLC) field-extension relation. DNA molecules attached to microspheres were anchored at a micro-nanofluidic interface and the molecules electrophoretically extended. We demonstrated that both the DNA segmental correlation and equilibrium lengths increased as the slit height decreased. Furthermore, for extremely confined DNA where $h \leq 30$ nm, we observed reptation of the DNAs' contours within the nanoslit, a phenomena that may be induced by inhomogeneous surface charge distributions. This nano-confined system may have implications for single-molecule sensors on detecting and analyzing genetic, epigenetic markers, and related nanobiotechnological applications.

5:20pm **BI+AS+NS-MoA11 Measuring DNA Looping Pathways using Nanofluidic Manipulation**, *M. Roushan, Z. Azad, H. Wang*, ***Robert Riehn***, NC State University

DNA performs a carefully choreographed ballet during the cell cycle. The organization is driven by the specific binding of proteins to form tertiary DNA-protein-DNA complexes. The search process that precedes the formation must overcome the challenge of very low effective mobility of genomic-sized DNA pieces in the dense cellular environment.

In this paper we will discuss a group of nanofluidic device that force two DNA molecules to either slide past each other in parallel, or cross over each other at a steep angle. Nanochannel cross-sections are 100x100 nm^2, and are hundreds of microns long. Because DNA is elongated through confinement, loop with a length down to 2 kb can be directly observed in real time. Channels are made of fused silica, enabling single-molecule observation of both DNA and proteins. Because the effective concentration of DNA inside channels exceeds 1 mg/ml with the channel at the point of DNA-DNA contact, protein-mediated capture cross-sections are very high.

We will present analyses of different DNA-binding proteins that demonstrate that we can distinguish dense and sparse binding modes and the compensation of electrostatic DNA-DNA repulsion through protein binding. We further report the detection of long-lived tertiary complexes acting as a lock for looped DNA configurations, and the presence of very short-lived transient links. We further demonstrate a pathway for loop formation that is enhanced in nanochannel devices, and that may be important in a cellular context. By using precision hydrodynamic flows, we are able to measure free energies of the search process.

Materials Characterization in the Semiconductor Industry Focus Topic
Room: 313 - Session MC+2D+AP+AS-MoA

Characterization of III-Vs (2:00-3:20 pm)/Photovoltaics, EUV masks, etc. (3:40-4:40 pm)

Moderator: Alain Diebold, SUNY College of Nanoscale Science and Engineering, Paul van der Heide, GLOBALFOUNDRIES, NY, USA

2:00pm **MC+2D+AP+AS-MoA1 High Resolution SIMS Depth Profiling in III-V Compound Semiconductors**, ***Marinus Hopstaken***, *M.S. Schamis, Y. Sun, A. Majumdar, C.-W. Cheng, B.A. Wacaser, G. Cohen, K.K. Chan, D.K. Sadana, D.-G. Park, E. Leobandung*, IBM T.J. Watson Research Center

Recently, there has been renewed technological interest for application of InGaAs and related III-V high-mobility materials as a potential replacement for the MOSFET Si-channel [1]. Successful integration of novel materials and processes requires accurate physical characterization of in-depth chemical distribution with nm-scale resolution. We will address some of the challenges regarding SIMS depth profiling of III-V materials and propose analytical solutions for the characterization of more complex multilayer substrates, impurities therein, and Ultra-Shallow Junction (USJ) doping profiles.

Ion beam based sputtering of III-V compounds is intrinsically more complex than in conventional Si substrates. One of the major issues with depth profiling of III-V materials is their higher sensitivity to formation of ion-beam induced topography, which has a detrimental impact on depth resolution [2]. We have previously reported anomalous sputtering behavior of (In)GaAs under low energy O_2^+ sputtering, causing severe degradation of depth resolution [3].

In case of low energy Cs^+ sputtering at oblique incidence, we have achieved uniform sputtering conditions on different III-V compounds with no significant topography formation. We have demonstrated constant depth resolution in III-V multilayer structures with decay lengths as low as 2 nm/decade at low Cs^+ impact energy (down to 250 eV).

We will address some of the analytical challenges regarding the quantification of depth and concentration scales in III-V multilayer structures, grown by hetero-epitaxy. We employ explicit corrections for yield variations using appropriate standards in their respective matrices. A special case occurs for the group IV *n*-type dopants (*i.e.* Si, Ge), which are typically monitored as negative cluster ion attached to the group V element for reasons of sensitivity. We have developed a quantification scheme to determine [Si] doping profiles in hetero-epitaxial structures, composed from the negative cluster ions (e.g. $SiAs^-$, SiP^-) in the respective matrices.

In summary, this work has improved our fundamental understanding of low-energy ion beam interactions in III-V materials, which is essential for achieving sub-nm depth resolution in thin-film structures. In addition, this work has provided with an optimum window of analytical conditions for quantitative analysis of a wide variety of impurities and dopants with high sensitivity in different III-V materials.

1. Y. Sun et al., *IEDM 2013 Conf. Proc.*, p. 48-51.

2. E.-H. Cirlin, J. J. Vajo, R. E. Doty, and T. C. Hasenberg, *J. Vac. Sci. Technol. A***9**, 1395 (1991).

3. M. J. P. Hopstaken et al., *J. Vac. Sci. Technol. B***28**,1287, (2012).

2:20pm **MC+2D+AP+AS-MoA2 Nitrogen Incorporation in Dilute Nitride III-V Semiconductors Measured by Resonant Nuclear Reaction Analysis and Ion Beam Channeling**, ***John Demaree***, *S.P. Svensson, W.L. Sarney*, US Army Research Laboratory

The behavior of dilute nitride III-V semiconductors depends critically on the number of nitrogen atoms residing substitutionally on Group V sites, and this small nitrogen incorporation may be used to tailor the optical bandgap for detection of electromagnetic radiation in future low-cost near-infrared imaging systems. In this study, films of GaAsN and GaSbN were synthesized using molecular beam epitaxy at various temperatures and growth rates, with the assistance of a nitrogen plasma source isotopically enriched with ^{15}N. The films were examined using x-ray diffraction, secondary ion mass spectroscopy, x-ray photoelectron spectroscopy, and resonant nuclear reaction analysis (RNRA) to assess the amount of nitrogen incorporation. Furthermore, RNRA measurements were combined with ion beam channeling methods to ascertain the fraction of incorporated nitrogen atoms residing on substitutional and interstitial lattice sites. The narrow energy resonance and corresponding high depth resolution of the nuclear reaction used (the 897 keV p,gamma reaction with ^{15}N) also enabled an assessment of the substitutional incorporation of the nitrogen throughout the thickness of the 100-400 nm thick films.

2:40pm **MC+2D+AP+AS-MoA3 Determination of Growth Conditions for Highly Mismatched Alloys, Using *In Situ* Auger Electron Spectroscopy and Flux grading**, ***Stefan Svensson***, *W.L. Sarney,* US Army Research Laboratory*, M. Ting, K.M. Yu,* Lawrence Berkeley National Laboratory*, L.W. Calley*, Staib Instruments, Inc.

The electronic band structures of GaN can be effectively modified by the incorporation of Sb. Because of the high electronegativity mismatch between Sb and N growth of GaNSb by molecular beam epitaxy (MBE) must be done at relatively low temperatures and under N-rich condition in order to control the bandgap of the material. The Sb-flux must also be chosen carefully in relation to the growth rate and N-overpressure to control composition and crystallinity. These growth conditions represent a vast parameter space, which is extremely time-consuming to explore in a systematic fashion.

The typical approach for attacking such a problem is to judiciously select a limited set of parameter combinations based on experience and literature data. However, if growth windows are narrow there is no guarantee for success. To more quickly cover a larger parameter range we have grown a very limited number of samples but continuously varied one parameter at a time while employing a combination of in situ and ex situ probes that can reveal critical parameter points. The most novel piece of equipment is the in situ *STAIB Auger Probe,* which allows uninterrupted chemical analysis during crystal growth. In all of the following experiments the substrate temperature was fixed at 325 °C.

In one experiment we determined the transition between Ga- and N-rich MBE growth conditions of GaN by setting a fixed N-flow that generated a steady-state background chamber pressure of $1.5x10^{-5}$ Torr, while the Ga-source was set up to generate a linear flux ramp from $9.8x10^{16}$ to $3.9x10^{18}$ $at/m^2/s$ over two hours. During this ramp, the Auger electron signals for N (375 eV), and Ga (1050 eV) were continuously monitored. As expected, both the Ga and N signals increased as a GaN film was starting to form under N-rich conditions and subsequently stabilized. At about 80 min the N-signal started decreasing, which we define as the boundary between N- and Ga-rich conditions and could thus determine the critical Ga-flux relative to the N gas-flow.

In a second experiment the previous information was used to set Ga- and N-fluxes to slight N-rich conditions, while the Sb-valve was slowly opened. In this case both the Auger signals and the reflection high-energy electron diffraction pattern were observed to find the transition between crystalline and amorphous growth conditions. The sample was subsequently analyzed with Rutherford backscattering, which verified the varying Sb-composition. With the data from these two test samples subsequent films were grown with the desired bandgap of 2.2 eV suitable as photoelectrodes for photoelectrochemical water splitting application.

3:00pm **MC+2D+AP+AS-MoA4 Electron Channeling Contrast Imaging: Examining Dislocation Effects in III-Ns**, *J.K. Hite,* U.S. Naval Research Laboratory*, P. Gaddipati,* American Society for Engineering Education*, **Michael Mastro**, C.R. Eddy, D.J. Meyer*, U.S. Naval Research Laboratory

III-N materials continue to play a significant role in a range of technologies from rf electronics to visible and UV emitters and detectors. This is true despite a heavy population of extended defects in the active regions of these devices, which degrade the operation, potential performance, and reliability of such devices. With such high dislocation densities when grown heteroepitaxially on sapphire or SiC (10^8-10^{10} cm^{-2}), techniques to reliably, rapidly, and non-destructively determine spatially defect density are necessary to determine the effects of these defects on device performance.

The most precise characterization tool for defect density has been transmission electron microscopy, but this is a destructive technique, as are other methods such as molten KOH or photo-electrochemical etching of the surface to reveal dislocation sites. Cathodoluminescence imaging only detects dislocations which change the optical emission of the material. X-ray diffraction can be used to extrapolate dislocation density, but not identify individual defects.

Electron channeling contrast imaging (ECCI), a non-destructive technique that has been used to examine defects in metals and ceramics, has recently seen use in III-nitride semiconductors. This technique allows for direct imaging of dislocations, grain boundaries, and topological information all at once. We will present an overview of the uses of ECCI in characterizing III-N materials, culminating in recent work applying the technique to AlGaN/GaN HEMT structures. By imaging the active areas of van der Pauw structures on a single sample with varying mobility, we find a direct negative correlation between screw dislocation and electron mobility.

3:40pm **MC+2D+AP+AS-MoA6 EUV Lithography Mask Cleaning Applications of TOF SIMS Analysis**, ***Thomas Laursen***, *S.W. Novak,* SUNY College of Nanoscale Science and Engineering*, A. Rastegar,* SEMATECH*, T. Nakayama*, SUNY College of Nanoscale Science and Engineering

Extreme-UV Lithography (EUVL) is the current R&D frontier for the semiconductor industry. Developing this new technology is generating new studies into a range of new materials issues. EUVL photomask is one important branch of this technology and serious issues have been identified related to the mask surfaces. Photomask performance is usually characterized in terms of EUV (λ = 13.5 nm) Reflectivity (EUVR) and absorption. But when it comes to surface degradation by radiation exposure and mask cleaning of defects, it is valuable to complement EUVR with a surface analytical technique in order to elucidate the material changes taking place. TOF SIMS has proven to be a versatile analytical technique in this regard. While it may not be the optimal technique in each and every case, it does provide high sensitivity to compositional changes and high-resolution depth profiles. Furthermore, TOF-SIMS analysis on the IonTof V-300 can be done using full-size photomasks which allow analysis at the various stages of processing.

The surface structures on the EUV mask surface consist of a stack of thin films having thicknesses ranging from 1 to 50 nm. The reflective layer contains 40 bilayers of Mo-Si consisting of 2.7 nm Mo and 4.1 nm Si—ending with a Si layer. This multilayer is usually capped with either a 2.5 nm Ru or in some cases a 2 nm TiO_2 surface film. Metallic films with high extinction coefficient with thicknesses in the range from 35 to 75 nm are deposited as an absorber layer and patterned on Ru-capped multilayer blanks.

The combination of EUVR and TOF-SIMS analysis of the Ru capped multilayer EUV masks and blanks provided detailed information on the effects of cleaning on contamination, materials degradation and oxidation. Whereas the EUVR measurements could be directly related to mask specifications, the TOF-SIMS analysis provided more detailed information on surface contamination and oxidation levels, as well as surface-film integrity.

The interactions of the various segments constituting a cleaning process have been characterized in terms of their effect on film etching and removals as well as film oxidation. In general sulfuric acid - H2O2 -based treatments caused a severe deterioration of the film structures, whereas NH4OH - H2O2 -based treatments (SC1) caused a more manageable deterioration. Current mask cleaning processes are therefore primarily based on SC1 cleaning. Another concern for mask defectivity is progressive defects generated by sulfate and ammonium compounds. TOF-SIMS was also used to study the aggregation of these compounds during electron irradiation (simulating EUV-irradiation conditions), which was visualized by stage-scan imaging.

4:00pm **MC+2D+AP+AS-MoA7 Characterization of Ag/CuInSe$_2$ Thin-Film Photovoltaics by Photoelectron Spectroscopy**, ***Pinar Aydogan***, Bilkent University, Turkey*, N. Johnson, A. Rockett,* University of Illinois at Urbana-Champaign*, S. Suzer*, Bilkent University, Turkey

Photovoltaic power source technology is one of the most desirable ways to provide energy for the world of tomorrow. Hence, it is important to understand the surface, electrical and photo-induced properties of these materials in order to enhance their efficiencies. Currently used materials in photovoltaic manufacturing technology are mainly crystalline silicon, CdTe (cadmium telluride), amorphous and nanocrystalline silicon, CIS (copper indium diselenide) and CIGS (copper indium gallium selenide). In this study, we focused only on the silver/copper indium diselenide cells, which contain a CdS layer on top. X-ray photoelectron spectroscopy (XPS) that we used for analysis was modified to apply both an external photo illumination and voltage bias during data acquisition. The first part of the research focuses on the result of photo induced variations in binding energies of elements and the main objective is to understand the different binding energy shifts of each element in the Ag/$CuInSe_2$ films in both wavelength- and intensity-sensitive fashion under illumination with three different continuous wave lasers. Furthermore, electrical charging properties of CIS/CdS thin film are studied with externally applied electrical square-wave pulses (SQW), so-called Dynamic XPS. Results will be presented with an ultimate aim of better understanding of the roles of defects affecting the performance of CIS devices. This work was supported by a joint NSF-TUBITAK collaborative research project (NSF Grant No: 1312539 TUBITAK Grant No: 212M051).

4:40pm **MC+2D+AP+AS-MoA9 Facile Synthesis of Composition Tuned Cu$_{1-x}$Zn$_x$O Nanoarchitecture on Alpha-Brass**, *Y. Myung, **Sriya Banerjee**,* Washington University, St. Louis*, H. Im, J. Park,* Korea University*, S. Raman,* Physical Electronics Inc.*, P. Banerjee*, Washington University, St. Louis

Composition controlled Cu$_{1-x}$Zn$_x$O layers have been synthesized on pretreated a-brass followed by ambient oxidation. The pretreatment consists of a vacuum anneal step which effectively depletes the surface of Zn. The depleted Zn specimens were then oxidized at various temperatures ranging from 300ºC – 600ºC. SEM and XRD result shows the oxide consists of CuO/ZnO film/nanowire composite architecture. The analysis of electronic structure (XPS) and optical properties (PL) shows the formation of Zn containing alloy in the surface region of CuO films. The composition ratio of Cu and Zn were calculated based on XPS survey spectra. In particular, XPS fine spectra revealed that as the oxidation temperature increases, the binding energy of Zn 2$p_{3/2}$shifts to higher energy, suggesting the possibility of hybridization between the Zn ions and Cu ions.

Photoelectrochemical properties of Cu$_{1-x}$Zn$_x$O cathodes exhibit robust photocurrent densities (~3 mA/cm^2). We suggest the dezincification followed by thermal oxidation provides a better approach for composition tuned nanostructure design and fabrication. These semiconductor nanoarchitectures are excellent candidate materials for fabricating solar energy harvesting photoelectrodes as well as optoelectronic devices.

5:00pm **MC+2D+AP+AS-MoA10 In-line Dimensional Measurement via Simultaneous Small Spot XPS and XRF for Cu CMP Process Control***, B. Lherron,* ST Microelectronics*, **Wei Ti Lee**,* Revera*, Motoyama, Chao, Deprospo, Kim*, IBM

As Cu lines used for CMOS devices interconnections become thinner and smaller, current metrology solutions reach their limits. XRay Photoelectron Spectroscopy (XPS) and XRay Fluorescence (XRF) are commonly used as Semiconductor manufacturing process control techniques to measure composition and/or film thickness. In this paper we are exploring the use of a combination of XPS and XRF collected simultaneously to measure the dimensions (line top CD, area and thickness) of Cu lines post Cu CMP on patterned structures. A set of structures with different Cu line width and pitch were used to demonstrate the capability of XPS/XRF on this new application. Results obtained showed good correlation with predicted CD measured by XPS and line section measured by XRF .The paper will also present the comparison with cross section as well as the performance in precision, sensitivity and accuracy of the newly developed technique.

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

5:20pm **MC+2D+AP+AS-MoA11 Imaging of the Native Inversion Layer on Silicon-on-Insulator via Scanning Surface Photovoltage; Implications for RF harmonic generation***, **Daminda Dahanayaka**,* IBM*, A. Wong,* Dartmouth College*, P. Kaszuba, L. Moszkowicz, R. Wells, F. Alwine,* IBM*, L.A. Bumm,* University of Oklahoma*, R. Phelps, J. Slinkman*, IBM

Imaging of the native inversion layer on Silicon-on-Insulator via Scanning Surface Photovoltage;

Implications for RF harmonic generation

Daminda Dahanayaka[1], Andrew Wong[2], Phil Kaszuba[1], Leon Moszkowicz[1], Randall Wells[1], Frank Alwine[1], Lloyd A. Bumm[3], Richard Phelps[1] and James Slinkman[1]

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One of the major challenges encountered during the development of IBM’s state-of-the-art RF CMOS Technology on Silicon-on-Insulator (SOI) was to overcome the adverse effects on the harmonic performance of stacked switch devices and transmission lines due to the presence of trapped positive charge, Q^+, at the interface of the buried oxide (BOX) and the underlying high-resistivity substrate (SX). Most commercially available standard SOI substrates for RF applications have specifications to maintain Q^+ less than 10^{11} cm^{-2}. The substrate resistivity for IBMs technology is specified to be greater than 1000 ohm-cm, (p-type), i.e. $p_0 \approx 5 \times 10^{13}$ cm^{-3}. This combination induces a “built-in” n-type inversion layer just under the BOX/SX interface. Using “Scanning Surface Photovoltage” (SSPV) microscopy, we present the first data to show quantitatively the extent of this inversion layer into the substrate. The technique disclosed here quantifies the inversion layer, the degree to which it can be suppressed, and has led to further enhancements to the RF technology on SOI, such as substantial NFET off-state leakage reduction.

References

[1] A. Botula et al., IEEE Topical Meeting on Silicon Monolithic Integrated Circuits in RF Systems, 2009. SiRF '09, 1-4 (2009).

[2] L.A. Bumm et al., US Patent No. 7,944,550.

[3] T. Ohno,IEDMTech. Digest, 627-630 (1995).

[4] J. Greco et al., US Patent No. 8299537 B2.

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.

[1] R. Caciuffo, E. C. Buck, D. L. Clark, G. van der Laan, MRS Bulletin **35**, 889 (2010)

[2] P. Santini et al., Rev. Mod. Phys. **81**, 807 (2009)

[3] H. C. Walker et al., Phys. Rev. Lett. **97**, 137203 (2011)

[4] Z. Bao et al., Phys. Rev. B **88**, 134426 (2013)

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[6] R. Caciuffo et al., Phys. Rev. B **81**, 195104 (2010)

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[8] N. Magnani et al., Phys. Rev. B **78**, 104425 (2008)

[9] H. C. Walker et al., Phys. Rev. B **83**, 193102 (2011)

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.

Applied Surface Science
Room: 316 - Session AS+BI+VT-TuM

Ambient Ionization Mass Spectrometry

Moderator: Gerardo Brucker, Granville-Phillips Vacuum Products, Steven Pachuta, 3M Company

8:00am **AS+BI+VT-TuM1 Laser Ablation Electrospray Ionization Mass Spectrometry with Ion Mobility Separation for Cell and Tissue Analysis**, ***Akos Vertes***, *B. Shrestha, H. Li, S.A. Stopka, L. Zhang*, George Washington University **INVITED**

Laser ablation electrospray ionization (LAESI) is a novel ion source that enables the direct analysis of biological samples, including tissues and individual cells. In this ionization method, mid-IR laser ablation is followed by electrospray ionization of the ablated material in the expanding plume. Molecular coverage in complex biological samples is limited, in part, by the large number of components and the absence of a separation step prior to ionization. In addition, isobars, such as structural isomers and conformers, are not distinguished by mass analysis alone. To overcome these limitations, LAESI is combined with ion mobility separation (IMS) before mass spectrometry (MS). In this contribution, we describe the first results with such a LAESI-IMS-MS system for metabolite, lipid and protein analysis, including its application to plant and animal tissues, MS imaging and single cell analysis. The studied systems, among others, comprise mouse brain sections, *Arabidopsis thaliana* leaves and green algae (*Chlamydomonas reinhardtii*) cell pellets. The introduction of IMS resulted in enhanced molecular coverage, reduced interferences, distinction of structural isomers, observation of larger multiply charged ions typically suppressed by singly charged abundant metabolites and phospholipids, and in extended dynamic range.

8:40am **AS+BI+VT-TuM3 Miniature Mass Spectrometry Systems with Ambient Ionization and MS/MS Capabilities**, ***Zheng Ouyang***, *L. Li, Y. Ren, X. Wang, X. Ma, R. Zou, R.G. Cooks, Y. Xia*, Purdue University **INVITED**

As a technique for chemical analysis, mass spectrometry is versatile and provides very specific information. High sensitivity can be achieved when sample matrix effect is properly suppressed. Miniaturization of the mass spectrometry instrument system and simplification of the operation procedure enable the chemical analysis outside the analytical laboratories and/or by personnel without special trainings. The development of these systems goes beyond the miniaturization of the mass analyzers and mass spectrometers. At Purdue, we have taken an approach of combining the ambient ionization for direct sampling and the miniature ion trap mass spectrometer with MS/MS capability. The miniature systems use linear ion traps (LIT) for mass analysis and can perform multi-stage MS/MS, which help to improve the specificity of the analysis using the fragmentation pattern of the target analyst and to eliminate the chemical noise from the complex mixtures. A discontinuous atmospheric pressure interface (DAPI) has been developed to allow coupling of ionization sources at atmospheric pressure with the instruments using miniature pumping systems to support the vacuum. The DAPI opens for about 20 ms for ion introduction and requires a 200 ms delay for pressure drop prior to mass analysis. The complex gas dynamics has been characterized using direct simulation Monte Carlo method and an electro-hydrodynamic simulation method has been developed for predicting the ion trajectory for DAPI instrument design. While mass spectrometers as light as 4 kg have been previously developed with capability of analyzing non-volatile compounds, two complete MS analytical systems have recently developed as the backpack MS for in-field analysis and the Mini 12 desktop system for point-of-care analysis by nurses and physicians. These two systems use ambient ionization for direct sampling analysis. The low temperature plasma (LTP) probe was modified with an in-line configuration for point-and-shoot operation with the backpack MS. New ambient ionization methods have been explored for development consumable sample cartridges for the Mini 12 system, which include the paper spray, extraction spray and the most recent slug flow microextraction nanoESI. IS-coated capillary samplers have been developed for highly quantitative analysis using several microliters of biofluid samples and extremely operation procedures. On-cartridge chemical derivatization has been developed to significantly improve the sensitivity of the target analytes in complex biological samples and on-cartridge assays have also been studied for direct monitoring the enzymatic functions. Direct analysis of the biological tissues have also been explored using Mini 12 and on-line Patenò-Büchi (P-B) reactions facilitated by UV irradiation has also been implemented to identify the locations of C=C bonds in the lipids, which is highly relevant to the biosynthetic pathways and the function of the lipids. The relative ratios of the unsaturated isomers can now be quantified, as the potential biomarkers for diagnosis of diseased tissues.

9:20am **AS+BI+VT-TuM5 The Importance of Sample Form and Surface Temperature for Analysis by Ambient Plasma Mass Spectrometry (PADI)**, ***Ian Gilmore***, *T.L. Salter, J. Bunch*, National Physical Laboratory, UK

Plasma sources for ambient mass spectrometry are of increasing importance owing to their ability to analyse a wide range of organics including polymers. Some industrially important molecules are not successfully analysed by electrospray based methods and here plasma methods are making an important contribution. For analysis in industry, it is essential to understand the fundamental mechanisms so that predictions can be made of which types of materials can and cannot be detected. In this study, we develop a metrology framework to understand the sensitivity of PADI to different substances and material form. We study in detail, the effect of sample temperature on the signal intensity and show that the intensity is proportional to the vapour pressure. Importantly, we also show the sample form, as a film or powder, has a strong effect of sensitivity. For the analysis of thin films at room temperature and using a low plasma power, a vapour pressure of greater than 10^{-4} Pa is required to achieve a sufficiently good quality spectrum. Using thermal desorption we are able to increase the signal intensity of materials with vapour pressures less than 10^{-4} Pa, in thin film form, by between 4 and 7 orders of magnitude. This is achieved by increasing the temperature of the sample up to a maximum of 200 °C. Thermal desorption can also increase the signal intensity for the analysis of powders. Prospects for imaging PADI and sub-micron imaging ambient mass spectrometry imaging will also be discussed.

9:40am **AS+BI+VT-TuM6 A VAMAS Interlaboratory Study for Desorption Electrospray Ionisation Mass Spectrometry (DESI MS) - Survey of the Measurement Issues**, ***Paulina Rakowska***, *E. Gurdak, F.M. Green, M.P. Seah, T.L. Salter, I.S. Gilmore*, National Physical Laboratory, UK

The DESI technique is celebrating a decade of application since its innovation in 2004. There has been significant progress in understanding its fundamentals and a rapid expansion in the applications, covering a diverse range of science and technologies. For wider uptake in industry, measurements need to be repeatable and constant. It is especially important to test that methods are transferable between different instrument designs and that analytical procedures are clear. This requires the development of a metrological infrastructure. Interlaboratory studies are an effective route to do this. VAMAS provides an excellent mechanism for such evaluation. Under this framework, the National Physical Laboratory (UK) has conducted a DESI interlaboratory comparison. The objectives of this study were to determine the current achievable repeatability and constancy of instruments. The comparison was conducted with the involvement of 20 laboratories from 10 different countries. The instruments used included 7 commercially made DESI sources with the remainder home-built. A variety of mass spectrometers were used including 13 Ion Traps, 4 Orbitraps and 4 Time-of-Flight. Participants were provided with an analytical protocol and two reference samples: a thin layer of Rhodamine B and a double-sided adhesive tape. The studies comprised acquisition of positive ion mass spectra in pre-determined *m/z* ranges. No sample preparation was required. Results for Rhodamine B show that intensity repeatabilities below 20 % may be achieved. However, inadequacies of the spray and sample stage designs lead to repeatabilities that average 50 % with some worse than 80 %. Rhodamine B is an excellent reference sample to check the sample erosion, the sample stage movement and memory effects. The adhesive tape samples show that the absolute intensity repeatability is 31 % with several achieving below 20%. Importantly, the spectral response, given by the relative repeatability, not measurable with Rhodamine B, was reduced to 9 % with a significant number achieving the 5 % expected of more mature analytical methods. The constancy of these spectra from relative intensities gives day-to-day averages of 31 %, over three times worse than the short term repeatability. Significant differences in the spectra from different laboratories arise from different factors. This first interlaboratory study has provided an effective survey of the measurement issues and some important conclusions can be drawn about the possibilities for DESI MS concerning overall practice, reference samples and recommendations for the future. These will be discussed.

11:00am **AS+BI+VT-TuM10 Mass spectrometry surface analysis outside the vacuum**, ***Justin Wiseman***, *M.E. ElNaggar, J.K. Kennedy, B.L. Laughlin*, Prosolia Inc. **INVITED**

Advances in mass spectrometry in the last 20 years has produced instruments with higher resolving power, smaller footprints, even portable, and the capability of measuring surfaces for molecules in the ambient air; the former truly enabling the latter. Ambient mass spectrometry involves the characterization of samples in their native state in the open air and is exemplified by the development of Desorption Electrospray Ionization (DESI) and Direct Analysis in Real Time (DART). DESI uses high velocity charged droplets produced by a pneumatically-assisted electrospray to effect desorption and ionization of surface-bearing analytes. The applications of the technique are broad and span from the detection of leachables to thin-layer chromatography to imaging of drugs, metabolites and lipids in histological tissue sections, where the lateral spatial resolution has been reported to be as high as 50µm. The flowprobe, also an ambient technique, uses a liquid-microjunction formed at the surface to extract and deliver analytes to the mass spectrometer via an electrospray source. The applications of the flowprobe are also broad and have included microarray sampling, thin-layer chromatography plate analysis, and biological tissue analysis. This presentation will discuss the merits and applications of each of the DESI and flowprobe devices, with emphasis on their application to imaging biological tissue.

11:40am **AS+BI+VT-TuM12 Transporting Ions from Ambient Pressure into Vacuum for Lab-based and Mobile Mass Spectrometers**, ***Mitch Wells***, FLIR Mass Spectrometry **INVITED**

The proliferation of Atmospheric Pressure Ionization (API) sources for mass spectrometry (MS) has expanded the applicability of the MS analysis technique to a wide range of chemical and biological challenges, to the extent that the 2002 Nobel Prize in Chemistry was awarded to John Fenn and Koichi Tanaka for their development of Electrospray Ionization (ESI) and Matrix-assisted Laser Desorption Ionization (MALDI), respectively. Furthermore, recent developments in a specific category of API, referred to as Ambient Ionization (AI), have simplified the applicability of API techniques by removing some or all of the need for sample preparation prior to analysis. AI techniques, such as Desorption Electrospray Ionization (DESI), Direct Analysis in Real Time (DART), and an ever increasing list of additional techniques and variations, allow for direct analysis of an enormous range of sample and matrix types; whole blood, illicit drugs in fingerprints, tissue cross-sections, pharmaceuticals, and forensic samples have all been examined with AI, to name just a relatively few examples.

All API techniques have in common the need to transport ions from atmospheric pressure into the high vacuum of the mass spectrometer - typically $<10^{-5}$ Torr (<1 mPa). Various ion sampling and transport mechanisms are used to transfer ions through differentially-pumped vacuum stages to the mass analyzer. In all cases, significant losses at each stage mean that only a very small fraction (<<1%) of the ions generated from a sample are actually analyzed. The situation is even worse for systems that are intended to be used in mobile or field labs, where space and power are at a premium and large pumping systems are therefore not acceptable.

This talk will briefly review AI techniques to illustrate their value in analytical chemistry (including biological, clinical, and forensic analysis), and will then describe means by which ions are transported from atmosphere into vacuum, with the hope of stimulating dialog with the vacuum community about ways and means that this process could be improved, especially for small, rugged instruments designed for outside-the-lab use.

Biomaterial Interfaces
Room: 317 - Session BI+AS+MN+NS-TuM

Biosensors
Moderator: Graham Leggett, University of Sheffield

8:20am **BI+AS+MN+NS-TuM2 An Inductive-Capacitive Sensor for Real-time Biofilm Growth Monitoring**, ***Ekaterina Tolstaya***, *Y.W. Kim, S. Chu, K.D. Gerasopoulos, W.E. Bentley, R. Ghodssi*, University of Maryland, College Park

We present a real-time biofilm monitoring device based on inductive-capacitive (LC) sensing principles. Bacterial biofilms cause severe infectious diseases and environmental contamination. The bacterial biofilm's complex structure and composition, as well as its ability to exchange genetic information, result in a high tolerance for antimicrobial agents. As a result, established biofilms on implanted or external biomedical devices, such as catheters, are difficult to treat. Traditional antibiotic therapies for biofilm infections often require doses 500-5000 times larger than for non-biofilm infections [1]. Moreover, biofilm growth in environmental and industrial facilities causes contamination and corrosion of equipment due to the toxins generated by biofilms. Therefore, early detection of biofilm growth is critical to facilitate treatment of severe infections and prevent equipment contamination.

In this work, an LC sensor was fabricated using conventional lithography and metal deposition via E-beam evaporation (Cr/Au, 15 nm/200 nm) (Figure 1). The resonant frequency of the sensor was approximately 16 MHz in air at room temperature. A device sensitivity of 1140 Hz/dielectric was demonstrated using a known dielectric material (deionized water) (Figure 2). *Escherichia coli* W3110 biofilms were grown for 48 hours over the LC sensor and the resonant frequency of the sensor was measured every 80 seconds using a spectrum analyzer (Figure 3). As the biofilm grew over the device, an increase in the resonant frequency of the LC sensor was observed. This is due to the lower dielectric permittivity of the biofilm compared to that of the growth media (Luria Broth, $\varepsilon \sim 80$), which results in decrease in the capacitance of the sensor. In control experiments with water and air as the media, a slight decrease in the resonant frequency was observed. The resonant frequency shift over time is in good agreement with the natural trend of biofilm growth (Figure 4) [2, 3]. The results validate the use of LC sensing for continuous monitoring of biofilm growth. This sensitive and reliable detection scheme, as well as the capability for flexible substrate integration and wireless interfacing, can serve as a foundation for the development of microsystems for real-time biofilm monitoring for both clinical and environmental applications.

8:40am **BI+AS+MN+NS-TuM3 The Interplay of Electrode Materials and Biomaterials in a Catechol-Modified Chitosan-Based Sensor for Clozapine Detection**, ***Robert Dietrich***, *T.E. Winkler, H. Ben-Yoav, S.E. Chocron, E. Kim,* University of Maryland, College Park*, D.L. Kelly,* University of Maryland School of Medicine*, G.F. Payne, R. Ghodssi*, University of Maryland, College Park

We present a study of atomic layer-deposited TiN and electroplated Pt black (PtB) as candidate electrode materials to replace Au in a catechol-modified chitosan redox cycling system (Fig. 1) for the electrochemical detection of the antipsychotic clozapine (CLZ). In complex biological fluids like blood, interference from other electrochemically active species is a major challenge. The choice of electrode material is critical in addressing this challenge, as surface morphology and composition may produce a stronger and more reproducible CLZ signal, while shifting that signal away from potential interferents and improving the signal-to-noise ratio. Our electrochemical characterization results indicate that TiN is superior to Au as a sensor material, with a 2.6 times higher CLZ signal and a 3.2-fold lower variability.

Identifying electrode materials with high CLZ signal-to-noise ratio will greatly aid in translating our detection approach into a point-of-care monitoring system. Such a device will reduce the burden currently associated with CLZ due to safety and efficacy monitoring requirements [1], thereby improving the quality of life for people affected by schizophrenia. Our previous work [2] has relied on gold electrodes as a substrate for our catechol-modified chitosan films. These 5×5 mm^2 micro-fabricated planar gold electrodes serve as controls, which we further modified here with: TiN for its inert properties; and PtB for its high surface area and potential electrocatalytic activity (Fig. 2).

The fabricated electrodes were characterized using cyclic voltammetry. Bare Au yields an oxidative CLZ peak signal of 1.06±0.20 µA, compared to 5.20±2.26 µA when coated with chitosan-catechol (Fig. 3). TiN electrodes produce a signal of 2.00±0.26 µA bare, and 13.7±0.7 µA when modified. The combination of higher signal and lower variability with the TiN is likely due to its inert chemical properties which also propagate more repeatable biomaterial modification. We observed a secondary peak with gold as well as bare TiN electrodes, likely due to interference related to chloride or oxygen. Modified TiN revealed only a single, CLZ-related peak. Results show that, as expected, signals from the bare PtB electrodes were 3370 times higher than from Au. However, they exhibited large variation between experiments, indicating the need for electroplating optimization. Testing the PtB electrodes with the chitosan-catechol film should increase both CLZ signal and resolution. Ongoing work is also focused on glassy carbon electrodes, which are expected to yield high repeatability by eliminating potential interfering oxygen signals in the redox cycling system.

9:00am **BI+AS+MN+NS-TuM4 Characterization of an Amperometric Glucose Sensor on a Flexible Polyimide Substrate for Continuous Glucose Monitoring and Insulin Delivery through Single Device***, X. Du, J.R. Motley, A.K. Herman,* **Liney Arnadottir***, G.S. Herman, X. Tan, J.F. Conley, Jr.,* Oregon State University*, W.K. Ward, R.S. Cargill, J.R. Castle, P.G. Jacobs*, Pacific Diabetes Technologies

Type 1 diabetes affects over one million people and every year more than 30,000 children and adults are diagnosed with type 1 diabetes in the United States alone. Patients with type 1 diabetes cannot produce their own insulin and depend upon glucose sensors to monitor their blood glucose and adjust insulin levels either by injection or an insulin pump. The continuous monitoring of glucose blood levels and automatic insulin release by an artificial pancreas is a promising alternative to current treatment options, and can significantly improve the comfort and quality of life for the patient. Here we introduce a flexible catheter with an integrated glucose sensor capable of both continuously measuring glucose levels and deliver insulin through a single catheter. The amperometric glucose sensor includes multiple Pt indicating electrodes, Ag/AgCl reference electrode, electrohydrodynamic jet (e-jet) printed glucose oxidase enzyme layers, and permselective membrane for optimal glucose response from the interstitial tissue. The compact design is integrated on a flexible polyimide substrate and requires high durability for all the components due to the small radius of curvature of the catheter. The e-jet printing provides digital patterning flexibility and highly precise deposition of the enzyme layer, which allows improved uniformity and accuracy of the glucose sensor. Here we will discuss characterization and optimization of the indicating and reference electrodes using electrochemical methods, scanning electron microscopy, X-ray photoelectron spectroscopy (XPS), and time of flight secondary ion mass spectrometry. XPS was used to confirm full glucose oxidase coverage of the indicating electrode. Electrochemical testing indicates that e-jet printed glucose oxidase inks are still active towards glucose oxidation after printing and subsequent deposition of the permselective membrane. The operation and characterization of a fully functional glucose sensor integrated onto a catheter will also be discussed.

9:20am **BI+AS+MN+NS-TuM5 Chemically Modifying Graphene for Biosensing and Interfacing with Biology***,* ***Paul Sheehan***, Naval Research Laboratory*, S.C. Hernandez,* National Research Council*, N. Long,* Nova Research*, S.P. Mulvaney, J. Robinson,* Naval Research Laboratory*, R. Stine,* Nova Research*, C.R. Tamanaha, S.G. Walton*, Naval Research Laboratory **INVITED**

Graphene has many properties that are highly suited for biological studies. For instance, its atomic thinness, high electrical conductivity, and simple production methods are ideal for biosensing. As another example, graphene can be attached to arbitrary substrates to lend them the chemical flexibility of carbon while adding only an ultrathin coating. For both biosensing and biofunctionalization, it is critical to produce high quality films that are precisely modified with the desired chemistry. For biosensing, the sensor must be functionalized for specific receptor-ligand recognition such as DNA-DNA or antibody-antigen binding. We will discuss our strategies for functionalization and the successful detection of specific DNA hybridization biologically-active field-effect transistors (BioFETs) based on chemically modified graphene. We will then discuss our use of graphene to interface biology with materials ranging from polymers to dielectrics to semiconductors. Graphene's incredible thinness enables its inclusion in more traditional sensing platforms as a non-intrusive functionalization layer, discreetly lending its chemical flexibility to other, more inert materials without otherwise impacting the sensing device.

11:00am **BI+AS+MN+NS-TuM10 Bioresorbable Sensors and Electronics**, ***John Rogers***, University of Illinois at Urbana Champaign **INVITED**

A remarkable feature of the modern integrated circuit is its ability to operate in a stable fashion, with almost perfect reliability. Recently developed classes of electronic materials create an opportunity to engineer the opposite outcome, in the form of devices that dissolve completely in water, with harmless end products. The enabled applications range from 'green' consumer electronics to bio-resorbable medical implants – none of which would be possible with technologies that exist today. This talk summarizes recent work on this physically 'transient' type of electronics and sensors, from basic advances in materials chemistry, to fundamental studies of dissolution reactions, to engineering development of complete sets of device components, sensors and integrated systems.

11:40am **BI+AS+MN+NS-TuM12 Surface Chemistry Enhanced Microbial Bioelectrocatalysis***,* ***Kateryna Artyushkova****, C. Santoro, S. Babanova, J. Cornejo, L. Ista, A. Schuler, P. Atanassov*, University of New Mexico

Bioelectrochemical oxidation carried out by bacteria attached on a solid electrode is capturing the attention of scientists all over the world. Different species of bacteria have been shown as electroactive and being able to oxidize organic compounds releasing electrons that can be transferred to a conductive solid support. If the oxidation reaction is coupled with the oxygen reduction reaction (ORR), the degradation of organics could lead to a production of useful electricity and water. Those related aspects are currently utilized in the development of alternative and cost effective bioelectrochemical systems (e.g. microbial fuel cell (MFC)) for simultaneous organics removal and electricity production. Understanding the bioelectrocatalytic nature of organics dissimilation by bacteria and the subsequent internal and external electron transfer is of a high importance for the further development of these systems and a key moment in their future application.

In this work, an artificial approach for enhanced microbial bioelectrocatalysis was explored along with study of the parameters promoting bacteria external electron transfer. This approach consisted of artificial modification of electrode surfaces having, as a result, different surface chemistries. Mixed bacterial culture development, biofilm growth and electrochemical performance have been studied. Smooth gold surfaces were modified with organic thiols to form self assembled monolayers (SAMs) with various functional groups (-CH_3, -OH, -$N(CH_3)_3$ and -COOH).

Power curves and single electrode polarization curves have been taken to evaluate the performance of the MFC as a whole and of the electrodes separately. XPS analysis of electrodes was used to study the effect of chemistry on the performance. Confocal and SEM microscopy was used to study the bacteria biomass and biofilm development was tracked over time .

Energy Frontiers Focus Topic
Room: 315 - Session EN+AS+EM+SE-TuM

Fuel Formation and Thermal Transport
Moderator: Michael Filler, Georgia Institute of Technology

8:00am **EN+AS+EM+SE-TuM1 Unraveling Thermodynamic and Kinetic Factors in Solar-Thermochemical Fuel Production**, ***Sossina Haile***, California Institute of Technology **INVITED**

Perhaps the greatest challenge facing our planet is sustainable energy. Given the vast solar energy resource base available to modern society, key to addressing this challenge is the conversion of solar energy into a storable form suitable for on-demand utilization. So emerges the concept of ‘Solar Fuels.’ Amongst many approaches currently pursued to generate solar fuels, thermochemical dissociation of water splitting is particularly attractive. It provides the benefits of full utilization of the solar spectrum and inherent temporal separation of hydrogen and oxygen gases. In recognition of these advantages, numerous multi-step cycles have been considered over the past several decades. Recently, two-step cycles making use of *non-stoichiometric* oxides have received attention because of the simplicity of their implementation. The approach relies on the large oxygen nonstoichiometry change that the material undergoes in response to variations in oxygen partial pressure (pO_2) and temperature (T). Specifically, upon exposure to high temperatures ceria undergoes reduction without change in crystalline phase to release oxygen. On cooling in the presence of H_2O (or CO_2), the oxide is reoxidized, releasing H_2 (or CO). The success of the method relies not only on favorable thermodynamics but also on facile kinetics, both in terms of surface reaction rates and bulk diffusion coefficient. Accordingly, we have undertaken a comprehensive study of ceria and its doped derivatives to assess both the equilibrium redox behavior by thermogravimetric methods and the kinetic response by conductivity relaxation methods. We find, for example, that introduction of Zr strongly increases the absolute non-stoichiometry of ceria, but at a penalty in terms of the sensitivity of the nonstoichiometry to changes in environmental conditions and in terms of bulk diffusivity. In another example, we find that the relaxation behavior of Sm-doped ceria is substantially more rapid than that of both undoped and Zr-doped ceria, a result that is tentatively assigned to differences in species mobilities. The implications of these fundamental differences in material properties for thermochemical fuel production are discussed.

8:40am **EN+AS+EM+SE-TuM3 Controlling Catalysis on Metal Nanoparticles by Direct Photoexcitation of Adsorbate-Metal Bonds**, *M.J. Kale, T. Avanesian,* University of California, Riverside, *H. Xin, J. Yan,* SLAC National Accelerator Laboratory, ***Phillip Christopher***, University of California, Riverside **INVITED**

Heterogeneous photocatalysis is typically assumed to occur via photon absorption by a solid-state photocatalyst (only the photocatalyst electronic states are involved in photon absorption) followed by charge carrier diffusion through the photocatalyst bulk and subsequent transfer to adsorbates. This process of energetic charge carrier generation and transfer results in wavelength dependent quantum efficiencies that strictly follow the absorption spectrum of the solid-state photocatalysts, regardless of the chemical transformation. The substrate (photocatalyst) mediated photo-absorption process inhibits approaches to control reaction selectivity by matching photon excitation wavelengths to bond specific electronic transitions, as typically done in molecular systems.

Here, we show that strong chemisorption bonds formed between CO and Pt metal surfaces can be activated with visible photons to drive catalysis through direct, resonant photoexcitation of hybridized Pt-CO states. This is enabled as the dominant photoexcitation mechanism (over substrate mediated photoexcitation) driving catalysis by using sub-5-nanometer Pt nanoparticle catalysts, where high surface area to volume ratios force photon absorption onto surface metal atoms. The direct photoexcitation process is observed to be significantly more efficient for driving photocatalysis than the indirect photoexcitation process when the energy of exciting photons is resonant with adsorbate specific electronic transitions involving hybridized metal-adsorbate states. It is also demonstrated that resonant photoexcitation of Pt-CO bonds on sub-5-nanometer Pt nanoparticles by visible light significantly enhances selectivity towards CO_2, over H_2O production, in the selective oxidation of CO by O_2 in an H_2 rich stream (also known as preferential CO oxidation). These results open new avenues to control catalytic reaction selectivity on sub 5-nm catalytic particles by resonant photoexcitation of adsorbate-specific electronic transitions involving hybridized metal and adsorbate states. It is expected that the development of insights into resonant electronic transitions between hybridized metal-adsorbate states should allow rational control of catalytic selectivity that cannot be achieved exclusively with thermal energy input.

9:20am **EN+AS+EM+SE-TuM5 Atomistic Insights as the the pH Dependence of Onset Potential of the Oxygen Evolution Reaction on Hematite**, ***Anders Hellman***, Chalmers University, Sweden

Hematite (α-Fe_2O_3) is an extensively investigated semiconductor for photoelectrochemical water oxidation, and recent research has shed light on many of the atomic processes involved. However, a controversy about the nature and role of surface states in the water oxidation reaction remains. Here first-principles calculations are used to investigate surface states present in hematite under photoelectrochemcial conditions. Most specifically a model describing how the onset potential for oxygen evolution reaction on hematite depend on the pH of the electrolyte is put-forth. The predictions of this model are confirmed to a high extent by measurements of the onset potential on hematite based model photoanodes. In particular, a linear dependence of the onset potential on the pH was observed, with a 49 mV / pH slope. Detailed photoelectrochemical characterization confirmed that the oxygen evolution reaction takes place via the same surface states irrespective of the pH. Moreover, the photovoltage and flat band potential of the hematite were also found to be pH independent. These results provide a framework for a deeper understanding of the OER when taking place on semiconductors (like hematite) via surface states

9:40am **EN+AS+EM+SE-TuM6 Rational Design of Pt_3Ni Alloy Surface Structures for Oxygen Reduction**, ***Liang Cao***, *T. Mueller*, Johns Hopkins University

A cluster expansion approach based on ab-initio calculations has been used to investigate the relationship between surface structures of $Pt_3Ni(111)$ alloy catalysts and their catalytic activity. With this approach, we build a direct bridge between the atomic structure and catalytic properties of Pt-Ni alloy system at a variety of compositions and chemical environments. The equilibrium near-surface structures are presented as a function of O_2 partial pressure and the chemical potential difference between Ni and Pt. We discuss the relative importance of strain, ligand, and ensemble effects in determining catalytic activity, and demonstrate how ensemble effects can be leveraged to rationally design alloy surfaces with optimal ORR activity by searching for surfaces with targeted oxygen binding energy.

11:00am **EN+AS+EM+SE-TuM10 Molecular and Mesoscale Design for Organic and Hybrid Thermoelectrics**, ***Rachel Segalman***, University of California, Santa Barbara **INVITED**

Thermoelectric materials for energy generation have several advantages over conventional power cycles including lack of moving parts, silent operation, miniaturizability, and CO2 free conversion of heat to electricity. Excellent thermoelectric efficiency requires a combination of high thermopower (S, V/K), high electrical conductivity (σ, S/cm), and low thermal conductivity (κ, W/mK). To date the best materials available have been inorganic compounds with relatively low earth abundance and highly complex, vacuum processing routes (and hence greater expense), such as Bi_2Te_3. Molecular materials and hybrid organic-inorganics bring the promise of solution processible, mechanically durable devices. While highly conductive polymers are now common place, they generally demonstrate low thermopower. Our work on molecular scale junctions that nanostructuring of organics allows them to act as thermionic filters between inorganic junctions which can lead to enhanced thermoelectric properties. We have taken inspiration from this fundamental understanding to design material systems in which we combine a high electrical conductivity, low thermal conductivity polymer with a nanoparticle that contributes high thermopower. Additionally, the work functions of the two materials are well-aligned which introduces the possibility of thermionic filtering at the interface and an additional boost to the power factor. The combination of these effects results in a new hybrid, solution processible material with a thermoelectric figure of merit within an order of magnitude of the Bi_2Te_3. In this talk, I will discuss both the use of thermoelectric measurements to gain insight to molecular junctions and how this insight translates to design principles for polymer and hybrid thermoelectrics.

11:40am **EN+AS+EM+SE-TuM12 Advances in Solid-State Energy Harvesting from Asymmetric Thermoelectric Devices**, *B. Cook,* ***Jay Lewis***, RTI International

The amount of thermal energy rejected as waste heat from industrial processes in the United States has been estimated at 32 quadrillion BTU per year, with an associated emission of 1,680 million metric tons of carbon dioxide. The ability to cost-effectively convert a portion of this thermal energy into useful electrical energy could improve energy efficiency, reduce operating costs, and decrease CO_2 emissions. Waste heat is typically categorized by temperature as high-grade (650ºC and above), medium-grade (232ºC to 650ºC, and low-grade (232ºC and below). In order to improve the thermal-to-electrical conversion efficiency of medium-grade waste heat, RTI has combined two different materials to form a high figure-of-merit, hybrid thermoelectric (TE) device. Recently-developed enhanced “TAGS-85”, or e-TAGS, was employed as the p-leg, while the n leg was comprised of improved half-Heusler (HH) material. This hybrid material pair provides a high ZT, lead-free TE material solution for waste heat recovery for use in vehicle or industrial platforms. The improved HH material employs two novel techniques to reduce thermal conductivity: (1) high-energy milling, and (2) addition of coherent inclusions. Single n-/p-couples were produced that achieved a 9.2% thermal to electric power conversion efficiency for $T_{hot} = 559°C$ and $\Delta T = 523K$. This is a significant efficiency improvement at a lower hot side temperature with the hybrid e-TAGS/HH single couple over the performance of a conventional, all HH couple. By optimizing the cross sectional areas of the pellets for equal heat flow, the resulting asymmetric couple achieved a conversion efficiency of 10.5% at $T_{hot} = 537°C$ and $\Delta T = 497°C$. A 49-couple hybrid module using HH materials paired with e-TAGS and operated with T_{hot} up to 600°C reached a maximum efficiency of 10%. The improved module efficiency is believed to be due to both improved materials and optimized cross-sectional area ratios between the n- and p- elements. We will also discuss additional advances in thermal to electric power conversion using multi-stage modules.

12:00pm **EN+AS+EM+SE-TuM13 The Effect of Particle Size and Surface Termination of n-Si on Thermal and Electrical Conductivity**, ***Thomas Lopez**, L. Mangolini,* University of California - Riverside*, S. Bux, J.P. Fleurial*, California Institute of Technology

A discussion of synthesis and characterization of bulk nanocrystalline silicon with grain sizes of around 20 nm and thermal conductivities as small as 100 mW/cmK at room temperature, will be presented. Nanostructured materials have great potential for thermoelectric applications because of the reduction in thermal conductivity due to phonon scattering at grain boundaries [1] and silicon is a well-understood, cheap, earth-abundant material. Other silicon nanostructures, such as nanowires [2], are being investigated as viable thermoelectric materials. We have used, for the first time, the combination of a non-thermal plasma process for the synthesis of silicon nanocrystals with hot pressing to produce bulk nanostructured silicon samples. The non-thermal plasma synthetic route has been proposed for the production of photo-luminescent silicon quantum dots with narrow size distribution (3 +/- 0.5 nm) [3]. The same reactor has been scaled up to produce silicon nanocrystals at a rate of hundreds of milligrams per hour. Silicon powder with sizes between 5 nm and 15 nm has been produced using either silane (SiH4) or silicon tetrachloride (SiCl4), which are low-cost silicon precursors. Results have shown surface termination of the non-thermal plasma synthesized particle, i.e. H or Cl, play a role in densification kinetics. Hot pressing is a high pressure, high temperature process that allows for the production of samples with bulk like densities while limiting grain growth. In this study we have produced bulk (12 mm diameter, 2-4 mm in thickness) samples of nanocrystalline silicon with relative densities exceeding 95%. Characterization by XRD and TEM confirms that grain sizes are around 30 nm. The effects of surface termination of nano-silicon on grain growth and grain boundary conditions will be extensively discussed.

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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^{o}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.

References

[1] J.A. Boscoboinik, X. Yu, B. Yang, F.D. Fischer, R. Wlodarczyk, M. Sierka, S. Shaikhutdinov, J. Sauer, H.-J. Freund, Angew. Chem. Int. Ed. 51 (2012) 24, 6005-6008. Angew. Chem. 124 (2012) 6107-6111.

[2] J.A. Boscoboinik, X. Yu, B. Yang, S. Shaikhutdinov, H.-J. Freund. Micropor. Mesopor. Mater. (2013) 165, 158-162.

[3] J.A. Boscoboinik, X. Yu, E. Emmez, B. Yang, S. Shaikhutdinov, F. Fischer, J. Sauer, H.-J. Freund. J. Phys. Chem. C (2013) 117, 13547-13556.

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 ($CeO_{\sim1.9}$) 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.

1. W. Jin, P.-C. Yeh, N. Zaki, D. Zhang, J. T. Sadowski, A. Al-Mahboob, A. M. van der Zande, D.l A. Chenet, J. I. Dadap, I. P. Herman, P. Sutter, J. Hone, R. M. Osgood, Jr., "Direct Measurement of the Thickness-Dependent Electronic Band Structure of MoS_2 Using Angle-Resolved Photoemission Spectroscopy." Phys. Rev. Lett. **111**, 106801 (2013)

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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.

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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 $1x10^{-4}$ 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.

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Biomaterial Interfaces
Room: 317 - Session BI+AS-TuA

Characterization of Biointerfaces
Moderator: Joe Baio, Oregon State University

2:20pm **BI+AS-TuA1 Comparative Study of the Bonding and X-ray Induced Reactions of Thiolated and Unthiolated DNA Adsorbed on Gold**, ***Richard Rosenberg***, Argonne National Laboratory, *J.M. Symonds,* Georgia Institute of Technology, *K. Vijayalakshmi,* Argonne National Laboratory, *D. Mishra,* Weizmann Institute of Science, Israel, *T.M. Orlando,* Georgia Institute of Technology, *R. Naaman*, Weizmann Institute of Science, Israel

High energy ionizing irradiation produces large amounts of low energy (<20 eV) secondary electrons (SEs). These electrons are produced via a cascade process following the ionization of a core (deeply bound) electron. Due to their low energy there is a high probability for the SEs to become trapped in antibonding orbitals, via resonant scattering, forming a temporary negative ion (TNI) resonance. If the lifetime of the TNI state is long enough, then bond rupture can occur by by a process known as dissociative electron attachment (DEA). There is vast literature on the role of TNI states and DEA in DNA related radiation chemistry.[1,2] Due to its high flux density, synchrotron radiation (SR) has often been used to induce and study radiation chemistry in numerous systems,[3] including DNA and related molecules. SR has also been used to probe the electronic structure and bonding of such molecules, primarily by probing the occupied states with X-ray photoelectron spectroscopy (XPS) and the unoccupied states with X-ray absorption (XAS) measurements. Bond overlap and localization can be revealed by XPS while XAS can determine the density of unoccupied states and the orientation of the orbitals. In this presentation we examine X-ray induced reactions of DNA adsorbed on a gold substrate when the DNA is either thiolated (tDNA) or when it is unthiolated (uDNA). By performing polarization-dependent XAS at the N K edge we determined that tDNA protrudes from the surface at ~45 degrees, in agreement with previous studies. We also found that the unthiolated molecules have a similar orientation. However, due to differences in charge transfer between the gold and the DNA in the two systems there is a higher density of unoccupied states in the N-C=N derived π* orbital for tDNA. We also found that the adsorbed tDNA has a significant higher cross section for radiation damage. The reason for this enhancement could arise from the greater probability of forming a TNI state for the tDNA due to the higher density of unoccupied π* states.

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2:40pm **BI+AS-TuA2 XPS Binding Energy Shifts for DNA Brushes on Gold**, *C.C.A. Ng*, ***Dmitri Petrovykh***, International Iberian Nanotechnology Laboratory, Portugal

DNA biointerfaces are important in a wide range of existing and emerging applications, such as biosensors, functionalization of nanoparticles for biomedical applications, and self-assembly of complex and functional nanostructures. The complexity of many of the DNA biointerfaces created for such applications often limits the ability to unambiguously interpret the results obtained from spectroscopy measurements for such systems. A powerful and successful approach to improving the analytical capabilities has been based on creating robust and well-defined reference systems, which then provide the insight for data interpretation in more complex analyses. Brushes of oligo(dT) single-stranded DNA can be attached to gold either via terminal thiol linkers, or via terminal blocks of (dA) nucleotides. While the former method results in a brush of roughly upright oligo(dT) strands relatively weakly interacting with one another, the complementarity of (dA) and (dT) blocks within the same strand creates a possibility of intra-strand hairpin-like hybrids in the (dA)-anchored case. Varying the parameters of these DNA brushes and deposition solutions creates a series with expected variation of thickness, surface density, and intra-strand interactions. Gold substrate provides a convenient binding energy (BE) reference for accurate XPS measurements of the characteristic DNA peaks. Following this approach, we find an unexpected BE shift of a N 1s peak across the series of DNA brushes. Typical effects observed in organic films do not appear to account for the full magnitude of the observed shift, so we will discuss the possible interpretations of this effect and its relation to the structure of DNA brushes.

3:00pm **BI+AS-TuA3 Simultaneous 3D Detection of Organics for Intact Samples with Infrared Spectromicrotomography**, ***Carol Hirschmugl***, University of Wisconsin Milwaukee **INVITED**

The holy grail of chemical imaging is to provide spatially and temporally resolved information about heterogeneous samples on relevant scales. Synchrotron-based Fourier Transform infrared imaging1 combines rapid, non-destructive chemical detection with morphology at the micrometer scale, to provide value added results to standard analytical methods. Hyperspectral cubes of (x,y, z, Abs (λ)) are obtained employing spectromicrotomography2, a label free approach, it inherently evaluates a broad array of wide organic materials, with minimal sample preparation and modification. Examples presented here (polymer composites, single cells and colonies of cells) demonstrate the broad applicability of this approach to detect complex chemical information of intact samples.

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Acknowledgements

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4:20pm **BI+AS-TuA7 Deep Thoughts: ToF-SIMS Profiling to New Depths**, ***Daniel Graham***, *L.J. Gamble*, University of Washington

The development of argon cluster sources has opened up new opportunities for ToF-SIMS depth profiling. These sources have enabled depth profiling of a wide range of materials that previously could not be accurately depth profiled. In addition, due to the low damage accumulation and sputtering efficiency of these sources, it is now possible to depth profile through microns of material. This in turn has opened up new opportunities for exploring the 3D chemical environments of a wide range of samples including drug eluting polymers, thick multilayer polymer films and porous tissue scaffolds. However, the ability to dig deeper into samples also results in significant challenges in 3D image reconstruction. For example, due to the fixed geometry of the analysis beam (at 45 deg from the surface normal in our instrument), sputtering away 1 micron of the surface will shift the analysis position by 1 micron. This means that if one were to depth profile 50 microns into a surface, the final image would be shifted by 50 microns. Traditional image registrations methods can be used to accommodate for these shifts, however when digging to depths larger than 10 microns, this requires significantly increasing the initial image size in order to end up with a usable image stack after the image shifting and cropping.

In this presentation we will summarize methods we have been developing to reconstruct deep depth profiles including adjusting the sample height during data acquisition and post acquisition image shifting. We will also show results from a new 3D image overlay tool that enables localization of different chemical environments in 3D and that can show areas of overlap between selected peak area images. These methods and tools will be demonstrated on data from control samples made from polymer beads on silicon and from data taken from polymer tissue scaffolds.

4:40pm **BI+AS-TuA8 Development of Novel Pharmaceutical Systems Through Characterisation**, ***David Scurr***, University of Nottingham, UK

The developments in pharmaceutical delivery systems such as injectable drug eluting microparticles [1], topically applied medicines [2] and wound dressings [3] can be utilised in areas such as the treatment of HIV, basal cell carcinoma and microbial infections respectively. In this study, the characterisation of such systems has been performed using time of flight secondary ion mass spectrometry (ToF-SIMS), x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM).

Injectable controlled release formulations were produced by spray drying two biocompatible polymers, poly(lactic-co-glycolic acid) (PLGA) and polyvinylpyrrolidone (PVP). The samples were analysed using a range of techniques including ToF-SIMS, XPS and AFM showing that the samples were hollow microparticles with a surface PLGA rich phase and an underlying PVP phase [1]. Additionally, more complex ternary systems incorporating PLGA, PVP and a poorly soluble investigational drug compound were also analysed. These studies highlighted the influence of sample processing parameters and drug concentration upon factors such as surface composition which is influential in the drug release properties of the systems.

The permeation of an antibacterial drug, chlorhexidine, into skin tissue has been illustrated using ToF-SIMS chemical imaging of cross-sectioned treated skin samples [2]. This methodology has been further applied to investigate the topical delivery of imiquimod, a drug used in the treatment of basal cell carcinoma. This work demonstrates the ability of the ToF-SIMS technique to correlate chemical species specific to the drug with physiological features within tissue cross-sections. Further application of ToF-SIMS chemical mapping has also been used to successfully differentiate chemically dissimilar regions of anti-microbial films which could be developed as wound dressing materials. Observations made for these materials using a combination of ToF-SIMS and AFM analysis revealed the distribution of the active agents upon the surface which would be relevant to the the anti-microbial performance.

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5:00pm **BI+AS-TuA9 Analysis of Peptide Microarrays on Si Using ToF-SIMS**, ***James A. (Tony) Ohlhausen***, *C. James,* Sandia National Laboratories*, D. Smith,* HealthTell*, S.A. Johnston, N. Woodbury*, Arizona State University

A microarray containing over 1200 each 200µm diameter spots consisting of various length peptide chain monolayers was analysed using Time-of-flight Secondary Ion Mass Spectrometry (ToF-SIMS). This peptide microarray was created using lithographic processes where chains of peptides were built one amino acid at a time. A silane coupling agent was used to attach the peptides to the oxide surface creating a monolayer of peptides directly bonded to the Silicon oxide surface. By tracking ion fragments corresponding to specific amino acids, usually immonium ions, we show that contrast consistent with the number of individual amino acid units in a given peptide dot is generally seen. While some immonium ions are not specific enough to generate clear contrast patterns, most can be used to verify the presence expected amino acids in each peptide dot. Additionally, some amino acids were not found to generate a specific fragment for identification in the positive secondary ion mode.

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5:20pm **BI+AS-TuA10 Investigating Tumor Microenvironments with ToF-SIMS**, ***Lara J. Gamble****, B. Bluestein, D.J. Graham*, University of Washington

Cancer is a heterogeneous malignancy that manifests itself in a variety of morphological types and clinical outcomes. Current evidence indicates that tumor metabolism plays a large role in cancer onset and progression, and its causes and effects are under intense scrutiny. Furthermore, it is of interest to know where changes in tumor metabolism occur within an affected tissue. However, there are few techniques that can specifically interrogate the tumor microenvironment. We use time-of-flight secondary ion mass spectrometry (ToF-SIMS) to determine differences in the chemical makeup of the tumor microenvironment of breast cancer tumor tissue samples. Human tissue biopsies from an ongoing trial have been subtyped using DASL genome assay and grouped into subtypes of Luminal B, Basal, and ERRB2. Images and spectra have been acquired on an IONTOF TOF.SIMS V using Bi_3^+. The ToF-SIMS information, combined with gene expression array analysis is used to investigate the chemical differences between chemotherapeutic resistant tumors and elucidate the underlying mechanisms. Using imaging ToF-SIMS the cellular and stromal regions within the tissue can be separated out as regions of interest (ROI). Imaging principal component analysis (PCA) was successful in separating cellular regions of the tumor and stromal regions when compared with a hemotoxylin and eosin (H&E) stained adjacent tissue slice. Using the ROIs identified from imaging PCA, we compare the chemical differences between cellular and stromal microenvironment chemistry. A comparison of spectral PCA using the entire analysis area vs spectral PCA of ROIs for cellular and stromal regions of the tissue is discussed. The chemistries of these subtypes are compared using ToF-SIMS image and spectral comparison from cellular and stromal regions. A spectral comparison of ROIs between tissue samples using PCA indicates that unique fatty acids distributions may relate to a tumor phenotype and chemotherapeutic resistance.

5:40pm **BI+AS-TuA11 Correlative Imaging of Mammalian Cells in Their Native Environments using a Microfluidic Reactor by ToF-SIMS and SIM**, ***Xin Hua****, C. Szymanski, Z.Y. Wang, B.W. Liu, Z. Zhu, J.E. Evans, G. Orr,* Pacific Northwest National Laboratory*, S.Q. Liu,* Southeast University, China*, X.Y. Yu*, Pacific Northwest National Laboratory

Mammalian cell analysis is of significant importance in providing detailed insights into biological system activities. Due to the complexity and heterogeneity of mammalian cell behavior and the technical challenge of spatially mapping chemical components in a hydrated environment, correlated chemical imaging from multiplexed measurement platforms is needed. Fluorescence structured illumination microscope (SIM), with super high resolution and visualization of proteins and sub-cellular structures in 3-D, provides more detailed information in cell imaging. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a unique surface-sensitive analytical tool that provides molecular information and chemical mapping with a sub-micron lateral resolution. However, the understanding of how the spatial heterogeneity and structural difference affect the mammalian cell activities in an unperturbed, hydrated state by ToF-SIMS is severely limited due to the challenge to detect liquids with high volatility under high vacuum environment using surface sensitive technique like ToF-SIMS.

We recently developed a novel microfluidic reactor for C10 mouse lung epithelial cell growth for SIM imaging and direct probing of hydrated cell in vacuum using ToF-SIMS. C10 cells were inoculated into the microchannel, incubated at 37 ºC for 24 hr., fed with 5 nM quantum dots, and then fixed with 4% paraformaldehyde before SIM imaging. In subsequent ToF-SIMS analysis, an aperture of 2 µm in diameter was drilled through SiN membrane to form the detection window to image biological surfaces directly; and surface tension is used for holding the liquid within the aperture.

SIM images show that C10 cells are successfully cultured on the SiN membrane, and quantum dots are uptaken by cells and dispersed in the cytoplasm. The ToF-SIMS *m/z* spectra showing characteristic fragments of dried cell sample, hydrated cells, and uninoculated medium in the microreactor will be presented. Moreover, 2D images of representative cell fragments and quantum dots ion mapping will be discussed. In addition, depth profiling will be used to provide time- and space-resolved imaging of the cells inside the microchannel. Furthermore, principal component analysis is conducted to evaluate the intrinsic similarities and discriminations among samples. Our results demonstrate feasibility for *in situ* imaging of cells in the hydrated state using ToF-SIMS for the first time. Correlative imaging using SIM and ToF-SIMS provides information across different space scales for investigating cell dynamics. This novel approach has great potential for studying intracellular processes in the future.

6:00pm **BI+AS-TuA12 Mass Spectrometry using Femtosecond Lasers and Postionization to Characterize Biomaterials Interfaces***, Y. Cui, Y.P. Yung,* ***Luke Hanley***, University of Illinois at Chicago

Secondary ion mass spectrometry (MS), matrix assisted laser desorption ionization MS, electrospray-based MS and other strategies are widely used for the analysis of intact bacterial biofilms, mammalian tissue, cell cultures, and their interfaces with biomaterials [Bhardwaj & Hanley, Nat. Prod. Rev. (2014) dx.doi.org/10.1039/C3NP70094A]. The combination of these desorption/ionization methods with high resolution MS and tandem MS capabilities permit metabolomic and proteomic imaging of such samples. Nevertheless, their use to detect many analyte classes within intact biological samples still often suffers from low sensitivity, selective ionization, and/or poor spatial or depth resolution. Laser desorption with ultrashort pulses can remove material from a solid with minimal damage to the remaining sample, potentially allowing both depth profiling and additionally, higher spatial resolution [Cui, *et al.,* ACS Appl. Mater. Interf. 5 (2013) 9269]. Furthermore, laser desorbed neutrals can undergo postionization by vacuum ultraviolet or ultrashort pulse radiation for subsequent detection by MS. Postionization has the additional advantage that proper selection of the delay time between the desorption and postionization laser can improve molecular analysis. Here, we demonstrate the small molecule imaging capability of these methods on intact, multispecies microbial biofilms and other complex organic/biological samples. Finally, comparisons are made to laser desorption MS under atmospheric pressure.

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:

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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.

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3. P. Jungwirth and D. J. Tobias, *Journal of Physical Chemistry B*, 2002, **106**, 6361-6373.

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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 distribu tions 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 el ementary energy loss lines from the distribution. Using this model, ac curate 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.

One of the authors, D. S., acknowledges funding from ARL W911NF-12-2-0041 and from NSF MRI-DMR-1337339

Thin Film
Room: 305 - Session TF+AS+EM-TuA

Thin Film: Growth and Characterization II
Moderator: Mark Davidson, University of Florida

2:20pm **TF+AS+EM-TuA1 A Statistical Optimization of Perpendicular Anisotropy and Damping for Ta-Inserted Double CoFeB/MgO Interface MTJ's**, *S. Gupta*, ***Samuel Schwarm***, *B. Clark*, University of Alabama

A statistical Design of Experiments was conducted on double-interface Ta-inserted CoFeB-MgO magnetic tunnel junctions (MTJ's). These MTJ's were deposited using a Shamrock planetary sputtering system. The thicknesses of the inserted Ta and the CoFeB electrodes were varied using Response Surface Methodology. The responses measured using magnetometry and ferromagnetic resonance were a) effective magnetization, b) damping constant and c) perpendicular anisotropy. The effect of annealing on the perpendicular anisotropy was also observed for these devices. As the Ta thickness is increased for fixed CoFeB thickness, the M-H loops indicate that the anisotropy is becoming perpendicular. After annealing, both magnetometry and FMR results show that the MTJ's indicate full perpendicular anisotropy. Interfacial perpendicular anisotropy, which can be extracted from the FMR measurements, scales with the inserted Ta thickness for both as-deposited and annealed samples.

2:40pm **TF+AS+EM-TuA2 1D Matlab Modeling of the Reaction-Diffusion System during the Selenization Process in the Two-Step CIGS Solar Cells Production Process**, ***Jurjen Emmelkamp***, *A. Mannheim*, TNO Technical Sciences, Netherlands

Introduction

In the two-stage fabrication process of CIGS thin-film solar cells first copper, indium and gallium precursor layers are deposited, followed by the selenization process where selenium vapor is provided at high temperature to form CIGS. Despite of the literature, many stages of the reaction-diffusion process are still a mystery. Several experimental techniques exist to analyze the selenization process, however, most of them are only useful to analyze the post-selenization product. In-situ XRD can be used to analyze the crystal structure during the selenization process, but the information is limited because depth profiles and amorphous intermediates are not measured. Modeling of the reaction-diffusion system during the selenization process can result in deeper understanding of the process and in a predictive model for the optimal process conditions that can lead to cheaper and more efficient CIGS solar cells.

The model

A relative simple 1D mathematical Matlab model is developed. Since many intermediate products and the CIGS end-product are crystals, and thus 3D systems, an 1D approach is very simplified. Intensive evaluation with experimental in-situ XRD and cross section EDX, as well as literature values, are used to tune the model specific parameters. Main parameters include diffusion and reaction constants of the different elements and binaries/ternaries, as well as the sticking factor at the surface for the uptake of selenium from the vapor phase. Using these parameters the (intermediate) reactions can be derived and fitted to the data from experiments and literature studies.

First the process temperature profile is calculated as function of time, followed by the calculating the uptake of selenium from the vapor phase. Additionally, the diffusion and reactions are modeled, using Fick's second law, error functions and multiple reflections at the solid interfaces. Based on phase diagrams the reaction kinetics of the most important reaction products are derived and are included into the model.

For reasons of memory limitations, the time and spatial mesh need to be relative coarse. For the spatial mesh this requires adaptive meshing, in order to adapt to small spatial variations and to mimic the overall and the specific layer growth well at small time changes.

Conclusions

The development of the model is still in progress, but the first results show good approximation of the selenium uptake and the formation of the first binaries and ternaries, such as $Cu_{11}In_9$, $Cu_{2-x}Se$, In_4Se_3 and InSe. This can be expanded easily to other intermediates, CIS, CGS and CIGS. However, further parameter fitting is required to mimic the experimental data better.

3:00pm **TF+AS+EM-TuA3 TiSiO Thin Films Deposited by Plasma Enhanced Chemical Vapor Deposition for Optical and Electrical Applications**, ***Antoine Goullet***, *S. Elisabeth, D. Li, M. Carette, A. Granier*, IMN, France **INVITED**

TiO_2 thin films are good candidates for the development of passive optical or electrical integrated devices. They exhibit high optical refractive index (1.8<n<2.7 at 633 nm) in combination with high transparency in the visible range and high dielectric constant (50<k<100). They are compatible with semiconductor technologies and can be synthesized at low temperature by plasma processes such as plasma enhanced chemical vapor deposition (PECVD). This technique is very attractive to tune film composition and properties such as film refractive index. PECVD is also known for its ability to prepare good quality amorphous or partially crystalline films at low temperature.

Titanium-silicon mixed oxide (TiSiO) materials can overcome some of the limitations given by TiO_2 material, e.g. columnar morphology and relatively low band gap energy.

In this study, TiSiO thin films are prepared without any intentional heating in low pressure inductively coupled discharges from titanium tetraisopropoxide (TTIP- $Ti(OC_3H_7)_4$) and hexamethyldisiloxane (HMDSO - $SiO_2(CH_3)_6$) precursors mixed with oxygen.

Structure and chemical composition of the films are investigated by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Information about film chemical bonds is also obtained from Fourier transform infrared spectroscopy (FTIR). Film morphology is characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Optical properties are mainly investigated by spectroscopic UV-Visible ellipsometry.

Capacitance-voltage (*C-V*) and current-voltage (*I-V*) measurements are performed by using MIS capacitors for evaluation of the mixed oxide film electrical performances.

TiO_2 thin films characteristics are investigated as a function of the plasma ion energy in the 25 – 175 eV range. Increasing the ion energy leads to more homogeneous and organized films with the transformation from anatase to rutile. To account for the columnar morphology of TiO_2 films, a gradient optical layer model was developed. The thin layer dispersion functions were described satisfactorily with the Tauc-Lorentz dispersion law.

TiSiO have been deposited by varying the HMDSO flow rate in the plasma operated in continuous or pulsed mode.

The thin films can be described as a mixture of silicon and titanium oxide at the atomic scale rather than two separate SiO_2 and TiO_2 phases. These mixed oxide layers are basically amorphous and exhibit good morphological properties provided the titanium content is lower than the silicon one.

On the whole these TiSiO layers offer a good compromise in terms of morphological, optical and electrical properties.

4:20pm **TF+AS+EM-TuA7 Kinetically-Limited Lattice Relaxation in Linearly- and Non-Linearly- Compositionally-Graded InxGa1-xAs/GaAs (001) Metamorphic Heterostructures**, ***Tedi Kujofsa***, *J.E. Ayers*, University of Connecticut

Metamorphic buffer layers allow tremendous flexibility to design novel InGaAs/GaAs semiconductor heterostructures for application in various microelectronic and optical devices. However, device fabrication, reliability and performance are limited by dislocation defects associated with the growth of highly mismatched systems such as InGaAs on GaAs substrate. Thus, understanding kinetically-limited lattice relaxation and development of a plastic flow model applicable to multilayered and compositionally graded heterostructure is desirable to provide guidance in designing InGaAs/GaAs devices. Previously, we reported a plastic flow model for ZnS_ySe_{1-y}/GaAs (001) heterostructures which predicts the non-equilibrium strain relaxation as well as misfit dislocation and threading dislocation densities. Here, we have extended our model to $In_xGa_{1-x}As$/GaAs (001) metamorphic buffer layers with arbitrary compositional grading profile. In addition, we have investigated the evolution of the kinetically limited in-plane strain of $In_xGa_{1-x}As$/GaAs (001) heterostructures with an emphasis on grading schemes employing a step, linear-, S- and power-law- lattice mismatch compositional profile. For each structure, we have studied the thickness and grading coefficient dependence on the average and surface kinetically-limited in-plane strain. In addition, we show that the use of compositionally graded buffer layers enables the design of $In_xGa_{1-x}As$/GaAs (001) heterostructures with high surface strain values which enhance the sweeping of threading defects and therefore yielding device structures with minimal defect.

5:00pm **TF+AS+EM-TuA9 Superconducting Properties of NbN and NbTiN Thin Films**, ***Matthew Burton***, *M.R. Beebe, R.A. Lukaszew, D. Beringer*, College of William and Mary

Thin films of NbN and NbTiN are promising materials currently researched for improvements in superconducting radio frequency (SRF) technology and applications. At present, bulk niobium SRF accelerating cavities suffer from a fundamental upper limit in maximally sustained accelerating gradients; however, a scheme involving multi-layered superstructures consisting of superconducting-insulating-superconducting (SIS) layers has been proposed to overcome this fundamental material limit of 50 MV/m [1]. The SIS multi-layer paradigm is reliant upon implementing a thin shielding material with a suitably high Hc1 which may prevent early field penetration in a bulk material layer and consequently delay the high field breakdown. It has been predicted that for thin superconducting films — thickness less than the London penetration depth (~200 nm in the case of NbN) — the lower critical field Hc1 will be enhanced with decreasing thickness. Thus, NbN thin films with a high Hc1 value are possible candidates for such SIS structures. We note though that since the intrinsic resistivity of NbN is rather large, efforts are also devoted to NbTiN which has similar superconducting properties but much lower intrinsic resistivity which is preferable for this application. Here we present our study on the structure and superconducting properties of a series of NbN and NbTIN thin films and correlate the effects of film microstructure and surface morphology on relevant superconducting properties such as the critical temperature, Tc, the lower critical field, Hc1, and the residual resistance ratio.

[1] A. Gurevich, Appl. Phys. Lett., 88, 012511 (2006).

5:40pm **TF+AS+EM-TuA11 High-Throughput Assessment of the Composition Dependence of Initial Passivating-Al_2O_3-Scale Establishment in $Al_xFe_yNi_{1-x-y}$ Alloy Thin Films**, ***Matthew Payne***, *J. Miller, A.J. Gellman*, Carnegie Mellon University, DOE - National Energy Technology Laboratory

AlFeNi-containing alloys capable of forming passivating Al_2O_3 scales are designed for high-temperature structural applications requiring robust oxidation resistance. Mechanical considerations typically dictate that Al content be minimized, but a critical concentration, $N_{Al}*$, is minimally required to promote the initial establishment of a continuous Al_2O_3 layer. Current understanding of how $N_{Al}*$ evolves across multi-component composition spaces is limited, being based largely on experiments that are constrained by the need for meticulous preparation and characterization of large numbers of single-composition samples. The study of properties across alloy composition space can be greatly accelerated using composition spread alloy films (CSAFs), materials libraries comprised of continuous lateral composition gradients. Properly designed CSAFs can contain every possible composition of a ternary alloy. In this work, ~120 nm-thick $Al_xFe_yNi_{1-x-y}$ CSAFs spanning the entire ternary range ($x = 0 \rightarrow 1$, $y = 0 \rightarrow [1-x]$) over an area of ~1 cm^2 were prepared. A variety of spatially resolved techniques were developed for effective, high-throughput characterization of early oxidation behaviors in the CSAFs. Energy-dispersive X-ray spectroscopy was used to measure changes in CSAF oxygen content as a function of both alloy composition and oxidation time. Raman spectroscopy allowed specific oxide phases formed in different regions of the composition space to be identified. X-ray photoemission depth profiling was performed at select locations of interest to determine composition and chemical state in CSAF cross-sections. These methods were used to study oxidation across $Al_xFe_yNi_{1-x-y}$ composition space in both dry and moist air at 700 K, and have enabled the identification of continuous boundaries separating regions of phenomenologically unique oxidation behaviors, including the $N_{Al}*(x,y)$ boundary for each environment. The results enhance fundamental understanding of early-stage $Al_xFe_yNi_{1-x-y}$ oxidation and can contribute to the accelerated design of next-generation alloys.

6:00pm **TF+AS+EM-TuA12 Structural, Electrical, and Optical Characterization of Impurity-Dependent, Ultra-Low-Dislocation-Density Ge Epitaxially Grown on Si and Characterization of MOSFETs Fabricated on Ge-on-Si**, ***Swapnadip Ghosh***, *S.M. Han*, University of New Mexico

Building on a simple two-step MBE growth technique, we have investigated possible dislocation locking mechanisms by dopant impurities, coupled with artificially introduced oxygen (O). In the case of n-type Ge grown on Si, our materials characterization indicates that the dislocation density (DD) can reach the ~10^5 cm^{-2} level, compared to p-type and undoped Ge on Si (GoS). We note that our Ge film covers the entire underlying Si substrate at the wafer scale without mesas or limited-area growth. In this presentation, we will focus on the use of n-type impurity (phosphorus) diffusion from the Si substrate and the introduction of O at the Ge-Si interface. The O is introduced by growing a thin chemical SiO_2 layer on top of the Si substrate before Ge epitaxy begins. Z-contrast cross-sectional TEM images suggest the presence of O precipitates in n-type Ge, whereas these precipitates appear absent in p-type Ge. These O precipitates are known to lock the dislocations. Supporting the argument of precipitate formation, the TEM shows Moiré fringes due to various phase boundaries that exist at the precipitate/Ge-crystal interface. We speculate that the formation of phosphorus (P) segregation resulting from slow diffusion of P through precipitates at the precipitate/Ge-crystal interface facilitates dislocation locking. Impurity segregation in turn suppress O concentration in n-type Ge leading to the reduced DD that appears on the top surface of n-Ge compared to p-Ge film. The O concentrations (10^{17} to 10^{18} cm^{-3}) in the n- and p-type GoS films are measured using secondary ionization mass spectroscopy. We have then compared the structural and electrical characteristics of n-type Ge films with its p-type counterparts. In n-type Ge, the DD decreases from ~10^9 cm^{-2} near the Ge-Si interface to ~10^5 cm^{-2} at the film surface. In contrast, we observe 5×10^7 cm^{-2} DD at the film surface in p-type Ge. The full width at half-maximum for our n-type Ge(004) XRD peak is 100 arcsec, compared to 230 arcsec of p-type Ge. As a stringent test of the dislocation reduction, we have also fabricated and characterized high-carrier-mobility MOSFETs on GoS substrates.We also report p- and n-MOSFETs with μ_{eff} of 401 and 940 cm^2/V-s and a subthreshold slope of 100 and 200 mV/decade, respectively.These effective mobilitiesshow an exceptional 82 and 30% improvement over that of conventional Si channel MOSFETs. We also investigate the optical quality of ultra-low DD GoS film by measuring photoluminescence (PL). Then-type Ge PL main peak shows pronounced tensile-strain (×0.8%) than that of p-type, which is an indicator of direct bandgap shrinking at the Γ band-edge.

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

Chemical Imaging in 2D and 3D
Moderator: Jeffrey Fenton, Medtronic, Inc., Kathryn Lloyd, DuPont Corporate Center for Analytical Sciences

8:20am **AS+BI+MC-WeM2 Expanded Approaches for Single Cell Analysis by SIMS**, ***Christopher Szakal***, National Institute of Standards and Technology (NIST)

Secondary ion mass spectrometry (SIMS) has been increasingly utilized for single cell imaging owing to its unique combination of spatial resolution and chemical differentiation by mass. Depending on the instrument type, subcellular lateral resolution between 10's and 100's of nanometers can be obtained, sometimes with both elemental and organic information obtained simultaneously, and sometimes with highly precise isotopic ratio measurements being attainable. However, imaging at the limits of the technique requires sufficient counts per pixel, which can be limited by analyte concentrations, competitive ionization pathways, and cumulative cluster ion beam damage accumulation. This work focuses on the advantages and disadvantages of combining focused ion beam (FIB) milling of single cells with subsequent ToF-SIMS imaging, as well as using large geometry (LG)-SIMS for high mass resolution analysis of single cell components that would otherwise not be easily detectable in other instrumental configurations. Such developments expand the research areas that are possible for single cell SIMS analyses, including cell differentiation without relying on multivariate analyses and targeted cell uptake studies.

8:40am **AS+BI+MC-WeM3 3-Dimensional Chemical Imaging on the Nanoscale with Cluster-SIMS**, ***Nicholas Winograd***, Penn State University **INVITED**

Bombardment of molecular solids with polyatomic projectiles allows interrogation of the sample with reduced chemical damage accumulation. Hence, it is now possible to perform depth profiling experiments with a depth resolution of less than 10 nm. In our hands, the projectile of choice is C_{60} due to the fact that the ion beam can be focused to a 250 nm spot size, and erosion of the sample can be performed with minimal chemical damage, especially at low temperature. With this combination of properties, it is feasible to think about creating 3-dimensional molecule-specific images.

A basic impediment to accomplishing this goal involves the fact that the SIMS images provide only chemical information and no direct depth information. The measureable quantity is the incident ion beam fluence, which can indirectly be related to depth, but independent measurements are required. The formation of topography and differential sputtering effects across the sample surface can also degrade the quality of the 3-D rendering when 2-D images are stacked. We have employed AFM in combination with SIMS imaging to develop protocols for correcting for these phenomena. Here, examples are shown using a patterned trehalose thin film and an Irganox delta layer reference material provided by NPL in the U.K. The idea is to provide chemical information with SIMS, and the depth information, acquired at each pixel in the image, using AFM. In addition to examining eroded craters directly, we have also developed a wedge-beveling technique that allows sputtering yield and topography to be determined with a single SIMS measurement and a single AFM measurement.

The long term aim of developing these protocols is to be able to acquire high resolution chemical images of single biological cells. So far, it appears that differential sputtering effects are not too serious for these samples. The combined SIMS/AFM strategy developed here will be important for verifying these initial observations. Finally, there is an emerging interest in gas cluster ion sources, namely Ar_{4000}, since even less chemical damage than C_{60} is observed, and the depth resolution during erosion appears to be less than 5 nm. Here we show that the combination of C_{60} imaging and Ar_{4000} sputtering provides an even more powerful protocol. In general, we show that the AFM/SIMS combination is a powerful tool for 3-dimensional chemical imaging.

9:20am **AS+BI+MC-WeM5 SIMS 2D and 3D Characterization of Organic/Inorganic Surfaces by FIB Crater Wall Imaging and Tomography**, ***Felix Kollmer***, *R. Möllers, D. Rading, S. Kayser,* ION-TOF GmbH, Germany, *N. Havercroft,* ION-TOF USA, Inc., *E. Niehuis*, ION-TOF GmbH, Germany

Information on the chemical composition, physical properties and the three dimensional structure of materials and devices is of major importance. Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) is known to be an extremely sensitive surface imaging technique which provides elemental as well as comprehensive molecular information on all types of solid surfaces. In the so-called dual beam mode the pulsed analysis beam is combined with a low energy sputter ion beam for the removal of material. This allows depth profiling of multilayers with high depth resolution as well as three-dimensional analysis.

However, the analysis of structures at greater depth (> 10µm) requires long measurement times and the build-up of surface roughness at the crater bottom limits the achievable spatial resolution. Moreover, extremely rough samples, samples with voids, and material that exhibits strong local variations in density or sputter yield are unsuitable for conventional depth profiling. Not only that the initial surface topography is unknown but it is also modified and in many cases even roughened by the sputtering process.

In order to overcome these limitations we used a combined SIMS/FIB setup. Either a Bi cluster beam or a mono-atomic Ga beam is used to FIB mill a crater into the sample. Subsequently, a 2D TOF-SIMS image of the vertical crater wall is acquired. Since the crater wall is hardly affected by the aforementioned roughening problems this approach allows the in-depth distribution of elements to be determined by analyzing a plane perpendicular to the surface at high lateral resolution (Dl<50nm) [1].

Moreover, by serial slicing of the crater wall followed by intermediate analysis steps this approach can be extended in order to provide the full 3D characterization of the analyzed volume. We will present 2D and 3D data of reference material, multilayer samples and technically relevant real world samples such as fuel cells and battery electrodes. For thin multilayer samples the FIB process can be performed under grazing incidence in order to bevel the surface and hence magnify and accentuate thin layers in the plane of the analyzed crater wall.

However, the FIB/SIMS approach fails when analyzing organic surfaces since the molecular structure is almost completely destroyed by the sputtering process. We will discuss methods to maintain the molecular structure under high dose sputtering conditions by performing the FIB milling with massive argon clusters.

[1] F. Kollmer, W. Paul, M. Krehl, E. Niehuis, SIMS XVIII proceedings paper, Surf. Interface Anal., 2012

9:40am **AS+BI+MC-WeM6 Multivariate Imaging: A New Approach towards Chemical State Identification of Novel Carbons in XPS Imaging**, ***Anders Barlow***, *N. Sano, P.J. Cumpson*, NEXUS, Newcastle University, UK

The differentiation between various forms of carbon in XPS spectra is made difficult by the subtle changes in C1s spectra that one would typically analyse. This is ideally demonstrated by a comparison of sp^2 and sp^3 carbon, such as graphite and diamond, where the variation in the C1s peak is less than 1eV. When applied to 'real' samples, such as a diamond like carbon coating, or a graphene surface, this difference can be even less. This presents a real problem for XPS imaging, where typically the analyst would sacrifice energy resolution in favour of signal intensity and spatial resolution. Such subtle differences are then completely lost when performing XPS imaging of novel carbon surfaces, where there may be discrete boundaries or layers between materials that are chemically very different, yet appear the same when the C1s peak energy is used in imaging.

We report a method of elucidating these differences in XPS imaging through shifting the focus from the C1s feature, to the X-ray induced Auger feature, a method we call Multivariate Auger Feature Imaging (MAFI). The carbon Auger feature can be studied and through the extraction of the so-called D-Parameter[1], chemical states of carbon can be clearly identified, with little ambiguity between sp^2 and sp^3 states. Extension of this method to XPS imaging, and the generation of 3-Dimensional images (2 spatial, 1 kinetic energy), we have shown that imaging of the Auger feature of graphite on polymers can identify multiple states of carbon-carbon bonding domains, where the imaging of the C1s feature alone yields no distinguishable differences or spatial features. We have also shown that PCA analysis of the carbon Auger feature also yields clear and distinguishable differences in the XPS images. The result is two independent methods of distinguishing novel carbon materials from one-another in XPS imaging. With modern instrumentation capable of a spatial resolution down to the few micron level, this greatly enhances the capability of XPS instrumentation to image novel carbon surfaces and devices.

[1] Lascovich, J.C. et al., App. Surf. Sci., 47(1), pp. 17-21 (1991).

11:00am **AS+BI+MC-WeM10 Multivariate Analysis Approaches for Image De-noising and Image Fusion**, ***Bonnie Tyler***, National Physical Laboratory (NPL), UK **INVITED**

Image fusion has become widely used in both medical diagnostics and optical remote sensing and there is growing interest in using these methods in applied surface science research. The goal of data fusion is to combine measurements from complementary techniques in order to aid in the analysis of the data and enhance information content. Recently, pan-sharpening techniques developed for optical remote sensing have received considerable interest in the surface science community because of their ability to improve spatial resolution and image contrast. Although image fusion can produce dramatic improvements in image sharpness and contrast, it can also lead to significant artefacts and care must be taken to ensure reliable results. These artefacts can be quite severe if the spectra have sharp bands, high background, or low signal-to-noise, features that are common in ToF-SIMS and XPS imaging. For optical remote sensing, a wide variety of methods have been developed for pan-sharpening, including approaches based on wavelet transforms, high pass filters, intensity hue saturation, Gram-Schmidt transforms, and Principal Components Analysis. Each of these methods offers advantages for certain applications but all are prone to artefacts when applied under non-optimal conditions. In order to minimize artefacts and produce reliable results, the methods must be adapted to account for the unique characteristics of different imaging modes. Of the methods in the literature, PCA image fusion is the most readily adapted for use with ToF-SIMS and XPS images. Methods for adapting PCA fusion for optimal use with ToF-SIMS and XPS images will be presented, including statistically based preprocessing of the data, target factor rotations and histogram matching. PCA image fusion can be a valuable technique for reducing noise, improving image contrast, and spatial resolution in ToF-SIMS and XPS data. With appropriate attention to the unique characteristics of each spectrometry, this can be done without significant artefacts or distortion of the spectral detail.

11:40am **AS+BI+MC-WeM12 Global Analysis Peak Fitting for Imaging NEXAFS Data**, ***Mark H. Van Benthem***, *J.A. Ohlhausen*, Sandia National Laboratory

We will present a method of analyzing NEXAFS image data to extract chemical information from the complex elemental peak structure in the material under analysis. The method, known as global analysis, fits emission bands to peaks described by nonlinear functions using nonlinear and linear optimization techniques. It can fit multiple types of peaks simultaneously, such as those found in NEXAFS spectra: Gaussian, Lorentzian, Voigt, asymmetric Gaussian and Lorentzian, and step edge with decay. Typically, peak fitting of NEXAFS data is very complex and somewhat arbitrary. Our method takes advantage of the high dimensionality of the image space to yield peaks with potentially greater reliability than single spectrum fitting. The method also employs data compression with principal component analysis (PCA) to rapidly complete the analysis. A discussion of the algorithm along with several examples of its application will be presented.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

12:00pm **AS+BI+MC-WeM13 Visualizing Pharmaceutical Compounds in Single-cells with label-free 3D Mass Spectrometry Imaging**, ***Melissa K. Passarelli***, *C. Newman,* National Physical Laboratory, UK, *A. West,* University of York, UK, *C.T. Dollery, I.S. Gilmore,* National Physical Laboratory, UK, *J. Bunch*, National Physical Laboratory

Drug-induced phospholipidosis is an adverse side-effect that hinders the therapeutic value of some pharmaceutical compounds. In this report, three-dimensional secondary ion mass spectrometry (SIMS) imaging was used to investigate the cellular uptake of phospholipidosis–inducing pharmaceutical compounds. A fast and simple sample preparation method, frozen dehydrated, was used to extract the drug compound to the surface layers of individual cells. Although the native localization of drug compound within the cell is lost, the compound was isolated to the confines of the individual cells and matrix-related effects were no longer a concern. With this method we were able to successfully detect intact-unlabeled drug compound at therapeutic dosages in macrophages. Relative quantification of the drug compound in individual cells was achieved. Overall, this approach provides a platform for studying cellular uptake of pharmaceutical compounds at the single cell level. This system also provides a model for studying metrology of cell imaging using SIMS. The effects of sample preparation and limitations of current technologies will be discussed along with new possibilities for the future.

Biomaterial Interfaces
Room: 317 - Session BI+AS-WeM

Nonlinear Optical & Vibrational Spectroscopy
Moderator: Luke Hanley, University of Illinois at Chicago

8:40am **BI+AS-WeM3 Characterizing Adsorbate Structure at the Solid-Liquid Interface through Nonlinear Vibrational Spectroscopy and Modelling Approaches**, *S. Roy, P.A. Covert, K.-K. Hung, U. Stege,* ***Dennis Hore***, University of Victoria, Canada **INVITED**

Even-order nonlinear spectroscopies such as second harmonic (SHG) and sum frequency generation (SFG) are valued for their sensitivity to interfacial structure as they are capable of discriminating from adjacent bulk phases based on symmetry. Visible-infrared SFG spectroscopy additionally harnesses the sub-molecular structural probe of a vibrational spectroscopy by tuning the infrared laser over molecular resonances. As a result, over the past two decades, SFG spectroscopy has been successfully applied to a wide variety of solid, liquid, and vapor interfaces, revealing signatures of the molecular organization that provide clues to the surface structure. Our group has been working on techniques to assist in the molecular interpretation of the SFG response. For small molecules, this includes grid computing-based searches to validate candidate orientation distributions based on the experimental data. For larger molecules with additional conformational flexibility, we employ molecular dynamics simulations to further refine our efforts to interpret the SFG data. Our most recent efforts explore the use of phase-resolved SFG spectra in order to develop more sensitive functions for scoring trial molecular orientation distributions. Our goal is to develop tools that are scalable to molecules of arbitrary complexity. This talk will provide some examples to illustrate our path towards this direction.

9:20am **BI+AS-WeM5 Vibrational Spectroscopy Investigation of the Giant Surface Potential of Organic Semiconductors**, ***Laura Kraya***, Princeton University, *C. Krekeler, C. Weigel,* Technical University Braunschweig, Germany, *P. Zhao,* Princeton University, *W. Kowalsky,* Technical University Braunschweig, Germany, *C. Lennartz,* BASF, *A.L. Kahn, B. Koel*, Princeton University

A phenomenon known as the giant surface potential (GSP), where the surface potential of organic films display linear growth with increasing film thicknesses in the absence of light was first reported by Ito et al. on (8 hydroxyquinoline)aluminum(Alq_3), a prototypical fluorescent material used in OLEDs. It has been shown that the surface potential of Alq_3 has reached 28 V for a 560 nm thick film by Kelvin probe measurements in vacuum in the absence of light. Since then this phenomenon has been observed for a broad range of molecules thermally evaporated on varying substrates under similar conditions. The effect is independent of the substrate, dependent on film thickness and decays quickly with illumination at the normal mode of the respective molecule. The spontaneous buildup of the GSP cannot be explained by any classical interfacial phenomena. Investigations into the cause of GSP, including the analysis of light and heat on the surface potential, are not yet understood.

In this study we use vibrational spectroscopy to understand the nature of the GSP buildup, where we have found a significant change in the vibrational structure of the organic material in thick films where the GSP is present as compared to thin films. The vibrational spectra of the most commonly studied light-emitting material, Alq_3, on indium tin oxide (ITO) is investigated as a function of thickness using high resolution energy electron loss spectroscopy (HREELS), Raman spectroscopy, high resolution x-ray photoelectron spectroscopy (HR-XPS), attenuated total reflectance infrared spectroscopy (ATR-IR), and density functional theory (DFT) calculations. In order to provide a holistic understanding of the GSP, the results are compared to the vibrational spectra of 1,3,5-tris(N-phenylbenzimiazole-2-yl)benzene (TPBi) on ITO, an electron transporter host material with a measured GSP of 0.07 V/nm, and bis(triphenylsilyl)-dibenzofuran (BTDF) on ITO, a typical electron-conducting host used in combination with hole-conducting deep-blue emitter with a measured GSP of 0.08V/nm. The observed spectra show significant changes with the presence of the GSP in the organic material on ITO, which can be explained in terms of different symmetries of the isomers as well as between complexes and isolated anions. Additionally, it has been found that the surface phase differs from the bulk phase, where a structured layer is evident at the interface of the organic semiconductor, and this layer shifts with increasing thickness and in the presence of the GSP. The present work has provided direct evidence that a different molecular orientation exists at the interface than in the bulk, where the GSP exists.

9:40am **BI+AS-WeM6 Diatom Biomineralization at the Molecular Level Probed by SFG Spectroscopy**, *H. Lutz,* Max-Planck-Institute for Polymer Research, Germany, *J.E. Baio,* Oregon State University, *V. Jaeger, A. Roehrig, G. Drobny, J. Pfaendtner,* University of Washington, ***Tobias Weidner***, Max-Planck-Institute for Polymer Research, Germany

Specialized mineral proteins control the growth of biogenic hard tissue. Using specific recognition motifs, proteins bind and release mineral facets and grow the intricate mineral morphologies found in Nature. Particularly fascinating examples of biomineralization are the high fidelity silica nanostructures in the shells of diatoms. Within the unicellular algae Cylindrotheca fusiformis, proteins called silaffin play a crucial role in the molecular biomineralization machinery. In order to harness the concepts used by Nature to efficiently fabricate mineral nanostructures we aim to understand the underlying protein–silica interactions. We found that artificial peptides consisting of lysine and leucine (LK peptides) can mimic silaffin's capability of forming various biosilica nanostructures. These peptides were designed to adopt helical or beta-sheet structures due to their hydrophobic periodicities and represent simple model systems to study the effect of protein folding on mineralization. Using surface sensitive sum frequency generation (SFG) vibrational spectroscopy we have studied the interactions of LK peptides with biosilica surfaces and within biosilica composites. We monitored how different LK peptides fold at the silica-water interface and we found that interfacial folding is crucial for the silica morphology: spheres, rods and flakes were produced by LKs – depending on their surface folding. Side chains also actively participate in the mineralization process. We probed the side chain structure of LKs in contact with silicic acid solution and observed increased ordering of charged lysine side chains during the formation of biosilica, indicating their involvement in silica nucleation. Combined with cryo-TEM measurements and MD simulations of different stages of nanoparticle nucleation the SFG studies provide important details of peptide-driven silica formation.

11:00am **BI+AS-WeM10 Water, Charge and Membrane Interface Stability**, ***Sylvie Roke***, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland **INVITED**

Life occurs in three dimensional turbid aqueous systems. A cell consists for ~60 % of water and contains many organelles and interfaces. The average distance between two molecules, or a molecule and a membrane interface is approximately 1 nm. The molecular, structural, dynamic, and biological properties of water, aqueous systems and aqueous interfaces are essential in understanding the complexity of life, and our ability to harness its features for novel (nano)technologies.

Here, I will introduce nonlinear light scattering methods that can be used to gain label-free molecular level information about model membrane interfaces in liquid aqueous nanoscopic systems. The use of these methods will be illustrated around the following questions:

· Does water behave charge asymmetrically?

· What is the role of water in determining the stability of amphiphilic interfaces?

· Is the molecular structure of model membranes influenced by the above considerations?

11:40am **BI+AS-WeM12 Second Harmonic Scattering: Characterizing the Interaction between Lipid Membranes and Water**, ***Cornelis Lütgebaucks***, *C. Macias-Romero, S. Roke*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland

Lipid membranes are essential for all organisms by separating functional compartments and mediating cellular signaling. Dioleoylphosphatidylcholine (DOPC) and Dioleoylphosphatidylserine (DOPS) are the main constituents of mammalian cell membranes. Molecular level understanding of cell membrane architecture often involves supported lipid membranes and invasive methods. We designed a second harmonic scattering (SHS) instrument that allows for investigating the molecular properties of interfaces from lipid vesicles in aqueous solution, label-free, and substrate independent. Characterizing DOPC:DOPS composed liposomes, we find that the water-lipid interaction is mainly responsible for the SHS signal. Moreover, the SHS signal increases up to a lipid mixing ratio of 9:1 and remains unchanged at lower ratios. This value coincides with the saturation value of DOPS in the outer leaflet of the mammalian membrane, when spontaneous apoptosis occurs.

12:00pm **BI+AS-WeM13 Analyzing the Structure of Amyloid Fibrils in Bacterial Biofilms *In Vitro* and in Real Time Using Sum-Frequency-Generation Spectroscopy**, *P. Johansson, R. Francisco, J. Bryers,* ***Patrick Koelsch***, University of Washington

Curli fimbriae are thin, needle-like structures formed by proteins. These so-called amyloid fibrils are typically associated with neurodegenerative conditions such as Alzheimer and Parkinson's disease; however, they can also play a beneficial role in various other processes in nature. *Curli fimbriae* have been shown to be involved in e.g. the colonization of abiotic surfaces, biofilm formation, and internalization of bacteria into eukaryotic cells. The structure of amyloid fibrils has been studied by IR spectroscopy, far UV CD spectroscopy, NMR, scanning probe techniques, and fluorescent probes that bind to fibrils. What is common to those approaches is the need for labelling or an *ex vitro* character, typically involving purification steps. Here we show how to use sum-frequency-generation (SFG) spectroscopy to study early stages of amyloid fibrillar formation within biofilms formed by a *Pseudomonas* strain of the *P. fluorescens* group. Studies have been performed *in vitro*, over several days of biofilm formation, under defined environmental conditions, and in real time - without the need for labels or any other disruptive sample preparation. In addition to the wild-type strain, genetically modified *P. fluorescence* were studied that are either overexpressing fibrils, or for which the fibrillar formation was suppressed. Furthermore, SFG spectra from purified amyloids were used to correlate *in vitro* and *ex vitro* results.

Energy Frontiers Focus Topic
Room: 315 - Session EN+AS+EM+SE-WeM

Thin Film Photovoltaics
Moderator: Rachel Morrish, Colorado School of Mines

8:20am **EN+AS+EM+SE-WeM2 Epitaxy and Nanochemistry of CdS on Cu(In,Ga)Se$_2$ for Photovoltaic Devices**, *X. He,* University of Illinois at Urbana Champaign, *H. Tellez, J. Druce,* Kyushu University, Japan, *K. Demirkan,* Miasole, *P. Ercius,* Lawrence Berkeley National Laboratory, *V. Lordi,* Lawrence Livermore National Laboratory, *J. Kilner,* Imperial College London, UK, *T. Ishihara,* Kyushu University, Japan, ***Angus Rockett***, University of Illinois at Urbana Champaign

Cu(In,Ga)Se$_2$ (CIGS) photovoltaics are very promising candidates for high-performance energy generation from sunlight. They typically include a heterojunction between CdS and CIGS. The nature of that heterojunction is critical to the performance of the devices. We present experimental results on the nanochemistry of CIGS and CIGS/CdS heterojunctions and the nanostructure of the junctions. In particular we present low energy ion scattering (LEIS) results on epitaxial single crystal CIGS and CIGS/CdS heterojunctions formed by chemical bath deposition of CdS. Also shown are results of high-resolution transmission electron microscopy (TEM) studies of the CIGS/CdS heterojunction where the junction is formed by physical vapor deposition. LEIS has single-atomic-layer chemical sensitivity that provides a unique ability to distinguish the nanochemical nature of CIGS surfaces and heterojunctions. TEM provides both nanostructural information and the possibility to determine the chemistry of the junction on the nanoscale by energy dispersive spectroscopy and energy filtered imaging. Complete epitaxy of the CdS throughout its ~50 nm thickness is observed in the physical-vapor-deposited CdS. Domains of cubic zincblende and hexagonal wurtzite structure CdS have been observed. Twins in the CIGS grains were found to propagate into and often through the CdS layer, resulting in a twin or grain boundary in the CdS. The CdS epitaxial relationship and the effect of surface steps on the CIGS surface are shown. The nanochemical analysis results show significant penetration of Cu into the CdS layer, although no alteration in the CdS nanostructure is observed. The other elements show an abrupt nanochemical junction. LEIS results show the presence of segregated layers on the CIGS surface and further refine the nature of the nanochemical intermixing across the interface.

8:40am **EN+AS+EM+SE-WeM3 Microstructure Development in Cu$_2$ZnSn(S$_x$Se$_{1-x}$)4 Thin Films During Annealing of Colloidal Nanocrystal Coatings**, *B.D. Chernomordik, M. Ketkar, K. Hunter, A.E. Béland,* **Eray Aydil**, University of Minnesota

A potentially high-throughput and inexpensive method for making Cu$_2$ZnSn(S$_x$Se$_{1-x}$)$_4$ (CZTSSe) thin film absorber layers for solar cells is annealing of coatings cast from colloidal dispersions of CZTS nanocrystals (NCs). The nanocrystal coatings can be annealed in sulfur or selenium atmosphere to make CZTS or CZTSSe, respectively. During annealing, the nanocrystal films can transform into polycrystalline thin films with micrometer size grains. Understanding the roles of key annealing parameters in the development of microstructure in CZTSSe thin films is critical for achieving inexpensive and high-efficiency CZTSSe solar cells. In this presentation, we will discuss the effects of parameters such as selenium vapor pressure, annealing temperature, substrate, and heating ramp-rate on the microstructure development in CZTSSe films and contrast the results with films annealed in sulfur. By using a closed system, rather than a flow furnace, we can quantify and systematically control selenium pressure. Annealing films at high selenium pressure (450 Torr) leads to the formation of a layer of 2-5 μm size CZTSSe grains on top of a nanocrystalline layer that is rich in carbon. This segregation of carbon at the CZTSSe-substrate interface is commonly ascribed to the immediate formation of a capping/blocking layer of CZTSSe grains, which trap the carbon, originating from the ligands on NC surfaces, beneath these grains. However, we found that a continuous layer of CZTSSe grains is not necessary to observe carbon segregation to the film-substrate interface. In contrast, films annealed with sulfur do not show such distinct carbon-rich layers and most of the carbon volatilizes from the film during annealing. Increasing the heating ramp-rate to the annealing temperature eliminates the formation the carbon-rich layer and results in grains that are approximately 500 nm. We will discuss the results of a series of experiments which led us conclude that Se condensation during annealing may play a key role in grain growth and carbon segregation.

9:00am **EN+AS+EM+SE-WeM4 Effect of Chemical Wet Cleaning on Surface Composition and Work Function of Thin Film CZTS,Se**, ***Kasra Sardashti***, University of California at San Diego, *E.A. Chagarov, T. Kaufman-Osborn,* University of California, San Diego, *S.W. Park,* University of California San Diego, *R. Haight, W. Wang, D.B. Mitzi,* IBM T.J. Watson Research Center, *A.C. Kummel*, University of California at San Diego

Polycrystalline Copper-tin-zinc-sulfide/selenide (CZTS,Se) compounds have received wide research interest due to their potential as inexpensive absorber materials composed earth-abundant elements. Photovoltaic devices fabricated on CZTS,Se has reached the highest (or record) conversion efficiency of the 12.6 %. One of the key parameters to further boost the conversion efficiency is to control the concentration of recombination sites at the surface, in the grain boundaries, and in the bulk. Surface states formed on the sample surface as a result of carbon and oxygen contamination can act as non-radiative recombination sites which limit the ultimate cell efficiency. Therefore, a surface-cleaning method which can effectively reduce the amount of surface oxygen and carbon is necessary for CZTS,Se processing. In this work, 2 μm thick CZTS,Se films were prepared by spin coating hydrazine-based precursor solutions onto Mo-coated soda lime glass substrates in a nitrogen-filled glove box. To clean the CZTS,Se surfaces, three different wet cleaning recipes were used: a) NH4OH only; b) HCl followed by NH4OH; 3) H2O2 followed by NH4OH. The effect of the wet cleaning on the surface composition including carbon and oxygen content has been studied via X-ray photoelectron spectroscopy (XPS) and femtosecond ultraviolet photoelectron spectroscopy (fs-UPS). Spatial variation of work function over the surface upon surface cleaning was measured via Kelvin Probe Force Microscopy (KPFM). The stability of the clean surface against reoxidation in ambient was modeled by density functional theory (DFT). The H2O2/NH4OH recipe showed the best result reducing the amount of surface O and C down to 5% and 20%, respectively. This is due to the oxidizing effect of H2O2 which converted the carbonaceous surfaces contaminants into oxides which were later removed by NH4OH. DFT calculations are consistent with a group VI surface being stable against oxidation by ambient moisture. KPFM measurements showed strongly non-homogeneous surfaces after both NH4OH-only and H2O2/NH4OH clean. Areas with work function different from CZTS could be the binary chalcogenides formed during the growth and were covered by the native oxide. NH4OH etch successfully removed the covering oxide and made those phases visible to KPFM.

9:20am **EN+AS+EM+SE-WeM5 Phase Transformation, Surface States, and Electronic Structures of Pyrite Thin Films Under *In Situ* Heating and Oxygen Gas Exposure**, ***Yu Liu***, *N. Berry, Y.N. Zhang,* University of California Irvine, *C.-C. Chen,* Argonne National Laboratory, *H. Bluhm, Z. Liu,* Lawrence Berkeley National Laboratory, *R.Q. Wu, M. Law, J.C. Hemminger*, University of California Irvine

Iron pyrite (cubic FeS_2) with its exceptional optical absorption and suitable band gap is a promising earth-abundant semiconductor for thin film solar cells. Using ambient pressure synchrotron x-ray spectroscopies, we report the nanoscale depth profiles of surface and electronic structures for phase-pure pyrite thin films under *in situ* heating and oxygen gas exposure. Polarized x-ray absorption spectra show that the absorption edge of Fe L_2-edge shifts closer to the Fermi surface with increasing temperature. The XAS line shapes of Fe and S *L*-edge provide the information of ligand crystal field environment and the phases of the FeS_2 particles. We also report the non-destructive photoemission depth distributions of sulfur defects, vacancies, impurities and oxide as a function of temperature and oxygen dose. Valence band spectra indicate a band gap narrowing related to the creation of surface states at elevated temperature. An irreversible phase transition from pyrite (FeS_2) to pyrrhotites ($Fe_{1-x}S$) occurs above 430 °C. In addition, our results under *in situ* oxygen gas exposure suggest that the surface monosulfide species is oxidized first, and the reduction in the total density of states near the Fermi surface is caused by oxide layers of sulfate like and iron oxide products on the top ~2 nm.

9:40am **EN+AS+EM+SE-WeM6 Improvement of SnS-based Photovoltaic Devices via Reverse Engineering of the V_{oc} and Study of Optimal n-Type Material**, ***Rona Banai***, *N.J. Tanen, J.J. Cordell, J.R. Nasr, R.E. Urena, H. Lee, J.R.S. Brownson, M.W. Horn*, Penn State University

Tin (II) Monosulfide (SnS) has theoretical promise as a new material for thin film photovoltaics (PV). Despite a full decade of rigorous research to develop SnS-based devices, improvement beyond single-digit percent efficiencies seems unattainable. Engineering this material into a usable device is crucial for future development. Our group has been investigating the optical and structural properties of magnetron sputtered SnS_x thin films [1,2,3] . This work will investigate the properties that govern open-circuit voltage, including band gap, series resistance, carrier concentration and built-in potential. Some of these parameters are directly related to the junction material paired with SnS. Several partner materials will be presented with p-SnS including, but not limited to highly doped n-ZnO and n-SnS. Current work is underway to produce n-type SnS as well which would have potential to produce a homojunction.

The optoelectronic properties of SnS make it a suitable material for PV. Its high absorption coefficient, greater than 10^4 cm^{-1}, and band gap near 1.3 eV are well matched with the solar spectrum. SnS also has a carrier concentration greater than 10^{15} cm^{-3} and potential to be both n-type and p-type. Our group is able to produce dense SnS thin films with optimal electronic properties. Sputtering the material gives great control over the material properties and recent work optimizing post-deposition heat treatment has shown great promise for improving the material.

Tin sulfide thin films were sputtered on glass and oxidized silicon substrates at varying substrate-to-target distances, substrate temperature, target power, and chamber pressure. The sputter target was a 3” SnS_2 with 99.999% purity (LTS Research Laboratories, Inc.). These sulfur-rich samples were then annealed under medium vacuum ($<2x10^{-6}$ Torr) in the deposition chamber at 400°C to produce a uniform α -SnS, which is most likely to be p-type. Producing n-type SnS is possible via annealing of the films in a methanol/$SnCl_4$ solution. Production of homojunction SnS-based thin film devices is not found in the literature. Our work aims to produce these devices for the first time and compare them to a well-known partner material such as ZnO.

[1] R. E. Banai, et al., in *Proceedings of 2012 38th IEEE Photovoltaics Specialists Conference*, Austin, 2012, pp. 164-169.

[2] R. E. Banai, et al., *IEEE Journal of Photovoltaics*, vol. 3, no. 3, pp. 1084-1089, 2013.

[3] R. E. Banai, et al., in *Proceedings of 2013 39th IEEE Photovoltaic Specialists Conference*, Tampa, 2013, pp. 2562-2566.

11:00am **EN+AS+EM+SE-WeM10 Advanced Contacts for High Efficiency CdTe Solar Cells**, *D. Meysing, J.J. Li, J. Beach, T.R. Ohno,* Colorado School of Mines, *M.O. Reese, T.M. Barnes,* National Renewable Energy Laboratory, ***Colin Wolden***, Colorado School of Mines

Record CdTe device efficiency has recently surpassed 20%, and it is the leading thin film photovoltaic technology in terms of commercial installation with current manufacturing capacity exceeding 1 GW/year. However, with a Shockley-Queisser limit of ~33% there remains substantial room for additional improvements in efficiency. The quality of both the front and back contacts has substantial influence on CdTe solar cells device efficiency, impacting the current and voltage respectively. This talk will focus on recent work directed at understanding the materials science of both the front and back contact interfaces and optimizing their performance.

Cadmium sulfide is the most commonly employed window layer in the front contact, and its properties can greatly affect cell performance through optical absorption and the quality of the CdS-CdTe junction. In this work, we develop reactive sputtering as an alternative to chemical bath deposition (CBD) for the production of oxygenated cadmium sulfide (CdS:O) to enable high efficiency CdTe solar cells. The intrinsic properties of CdS:O as well as their impact on device performance were studied by varying the oxygen content in the Ar sputtering ambient over the range of 0–10%. XRD, RBS, XPS, and spectrophotometry were used to measure the crystal structure, composition, bonding, and optical properties, respectively. The variation in properties is unsurprisingly non-linear, and optimal performance is attributed to a compromise between optical transmission, which improve monotonically with oxygen content, and band alignment which sharply attenuates device performance beyond a critical threshold.

It is notoriously difficult to make a good ohmic contact to CdTe using conventional metals, because this requires a work function of greater than 5.7 eV. Copper-doped zinc telluride (ZnTe:Cu) is one of the most commonly employed buffer layers to mitigate this issue. ZnTe was identified due to its valence band alignment and compatibility with CdTe. Copper has both positive and deleterious effects and it is critical to precisely control both its amount and spatial distribution in order to obtain high efficiency. We have developed a back contacting procedure that employs rapid thermal processing (RTP) to deliver precise control over the activation and distribution of Cu. The RTP process is coupled with atom probe tomography and advanced optoelectronic characterization to improve our understanding of the structure-property-performance relationships in this system. The advances achieved here using commercially scalable processes are combined to produce devices with V_{oc} > 850 mV and efficiencies exceeding 16%.

11:20am **EN+AS+EM+SE-WeM11 Structural Variations and their Effects on the Fundamental Bandgap of $ZnSnN_2$**, ***Nathaniel Feldberg***, University at Buffalo-SUNY, *Y. Yang,* University of Michigan*, W.M. Linhart, T.D. Veal,* University of Liverpool, UK*, P.A. Stampe, R.J. Kennedy,* Florida A&M University*, D.O. Scanlon,* University College London, UK*, L.F.J. Piper,* Binghamton University*, N. Senabulya, R. Clarke,* University of Michigan*, R.J. Reeves,* University of Canterbury, New Zealand*, S. Durbin*, Western Michigan University

In recent years $Zn-IV-N_2$ compounds have seen increased interest as potential earth abundant element semiconductors for photovoltaic and solid state lighting applications. Several reports of successful growth for the Ge and Si containing compounds are extant as well as more recent publications on the Sn containing member of the family. This material offers a possible alternative to indium containing materials which have experienced large price fluctuations due to limited domestic supply, lack of recycling and heightened demand. Our films were grown by plasma assisted molecular beam epitaxy on (111)-yittria stabilized zirconia. In the case of an ordered lattice, density functional theory (DFT) predicts an orthorhombic structure; however, the disordered lattice is predicted to be pseudo-hexagonal. Reflection high energy electron diffraction patterns for these films indicate single crystal structure with hexagonal symmetry, consistent with X-ray diffraction measurements. Hall effect indicates carrier concentrations in the $3\text{-}10x10^{21}$ cm^{-3} range for which we would expect a significant Burstein-Moss shift. Contrary to expectations, optical measurements of absorption onset occur at higher energy in films with lower carrier concentrations. As in $ZnSnP_2$, the bandgap is expected to narrow with the introduction of disorder for this material; this narrowing behavior is consistent with observed variations in absorption spectra. Of practical interest is the possibility of a material with a tunable bandgap without the need for traditional alloying. $Zn-Sn-N_2$ is expected to have a bandgap varying from 1.1 to 2 eV controlled by the continuous degree of order in the cation sub-lattice. Although hard X-ray diffraction measurements of these films do not show any variation from a hexagonal structure, Hall measurements of carrier concentrations compared with absorption data indicates that our samples vary their absorption onset, not as would be expected from Burstein-Moss Shift, but in a manner consistent with a variation in the lattice order. DFT calculations indicate that there is a variation in the Density of States between the ordered and disordered films. Films which were consistent with increased order absorption are also consistent with an increased order density of states measured by HAXPES.

This project is supported by NSF grant DMR1244887 (Program Director Charles Ying), and EPSRC grant EP/G004447/2 .

11:40am **EN+AS+EM+SE-WeM12 Inhomogeneity of *p-n* Junction and Grain Structure of Thin Film CdTe Solar Cells Studied by Electron Beams**, ***Heayoung Yoon***, *P. Haney,* NIST, *P. Koirala,* University of Toledo, *J.I. Basham, Y. Yoon,* NIST, *R.W. Collins,* University of Toledo, *N.B. Zhitenev*, NIST

Thin film CdTe solar cells are a promising photovoltaic (PV) technology in today's market due to their high optical absorption and inexpensive fabrication processes . However, the current module efficiency is well below the theoretically estimated maximum efficiency (13 % *vs*. 30 %) . Recent studies have suggested that inhomogeneity of the PV materials is mainly responsible for the low power conversion efficiency. In this work, we investigate the variation of local PV properties of CdTe solar cells, focusing on grain bulk, grain boundaries, and *n*-CdS / *p*-CdTe junctions. The window (≈ 120 nm thick CdS) and absorber (≈ 2.2 µm thick CdTe) layers were sputtered on a TCO (transparent conductive oxide) coated glass substrate followed by $CdCl_2$ treatment. The back contact metals (3 nm Cu / 30 nm Au) were deposited and annealed, creating 256 devices in a 15 cm by 15 cm solar panel. Following light and dark current-voltage measurements, we performed local characterizations using electron beams for high (> 13 %) and low efficiency (< 6 %) devices within the panel. Electron beam induced current (EBIC) was used to measure the local carrier collection efficiency with a spatial resolution of ≈20 nm exciting carriers either from the top surface or the cross-sections of the devices. Cross-sectional EBIC data reveals that the peak of efficiency is in the middle of CdTe layer in the low efficiency devices, while the carrier collection is maximal near the *p-n* junction in the high efficiency devices. The EBIC contrasts at grains/grain boundaries in these devices are also compared. The measured local electronic properties are correlated to microstructural morphology (Transmission Electron Microscopy), orientation (Electron Back Scattered Diffraction), and chemical composition (Energy Dispersive X-ray spectroscopy). We perform 2D model drift-diffusion simulations to determine the magnitude of downward band-bending near grain boundaries (with typical magnitude of 0.2 eV). We will discuss the impact of carrier generation rate (high level injection *vs*. low level injection) in EBIC analysis.

12:00pm **EN+AS+EM+SE-WeM13 Micro-Structural Activation Mechanisms in Thin Film CdTe Photovoltaic Devices**, ***John Walls****, A. Abbas, J.W. Bowers, P.M. Kaminski,* Loughborough University, UK*, K. Barth, W. Sampath*, Colorado State University

Thin Film CdTe photovoltaics is a commercially successful second generation technology now used extensively in solar energy generation at the utility scale. Although the cadmium chloride treatment is a process that is essential to produce high efficiency devices, the precise mechanisms involved in the re-crystallization and associated improvement in electronic properties have not been fully understood. In this paper we report on the application of advanced micro-structural characterization techniques to study the effect of the cadmium chloride treatment on the physical properties of the cadmium telluride solar cell deposited by both close space sublimation (CSS) and magnetron sputtering and relate these observations to device performance. In particular, High Resolution Transmission Electron Microcopy (HRTEM) reveals that the untreated material contains high densities of planar defects which are predominantly stacking faults and that the optimized cadmium chloride treatment removes these completely with only twins remaining. Parallel theoretical studies using Density Functional Theory (DFT) shows that certain types of stacking fault are responsible for the poor performance of the untreated material. Extending the treatment time or increasing the annealing temperature above ~400^0C improves the microstructure but results in lower efficiency devices. Composition –depth profiling using XPS and SIMS reveals that this deterioration in performance is linked with chlorine build up at the CdS/CdTe junction. These experiments and parallel theoretical studies have improved our understanding of the mechanisms at work in the cadmium chloride assisted re-crystallization of CdTe and could lead to further increases in device efficiency

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:

1. L.W. Liu, K. Yang, Y.H. Jiang et al., Scientific Report 3, 1210 (2013).
2. L. Gao et al., Phys. Rev. Lett. 99, 106402 (2007).

*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]

[1] Brune et al., Phys. Rev. Lett., 68, 624 (1992). [2] Komrowski et al., Phys. Rev. Lett., 87, 246103 (2001).[3] Schmid et al.,Surf. Sci., 478, L355 (2001). [4] Kurahashi et al., Phys. Rev. Lett., 110, 246102 (2013)

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.

[1] C. Klingshirn, *physica status solidi (b)* **2007**, *244*, 3027-3073.

[2] J.-C. Deinert, D. Wegkamp, M. Meyer, C. Richter, M. Wolf, J. Stähler, *Physical Review Letters* **2014**, *113*, 057602.

[3] H. Sezen, M. Buchholz, A. Nefedov, C. Natzeck, S. Heissler, C. Di Valentin, C. Wöll, *Sci Rep-Uk* **2014**, *4*, 3808.

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.

[1] T.L. Einstein, A. Pimpinelli, Diego Luis González, J. Crystal Growth (2014), http://dx.doi.org/10.1016/j.jcrysgro.2014.01.053.

[2] A. Pimpinelli, L. Tumbek, A. Winkler, J. Phys. Chem. Lett. 5 (2014) 995.

[3] A. Winkler, L. Tumbek, J. Phys. Chem. Lett. 4 (2013) 4080.

[4] A. Pimpinelli, J.R. Morales-Cifuentes, T.L. Einstein, preprint.

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.

[1] J. Tersoff, *Phys. Rev. B***39**, 5566 (1989).

[2] S. Munetoh, T. Motooka, K. Moriguchi and A. Shintani, *Comput. Mater. Sci***39**, 334 (2007).

[3] Q. Li, J. L. Krauss, S. Hersee, and S. M. Han, *J. Phys. Chem. C* 111, 779 (2007).

[4] D. Leonhardt and S. M. Han, *Surf. Sci.* 603, 2624 (2009).

[5] M.E. Kavousanakis, R. Erban, A.G. Boudouvis, C.W. Gear, I.G. Kevrekidis, . (2007) 382-407.

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).

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

Properties of 2D Materials
Moderator: Guy Le Lay, Aix-Marseille University

2:20pm **2D+AS+EM+MI+MN+NS+TF-WeA1 Tuning Excitons in Two-Dimensional Semiconductors**, ***Kirill Bolotin***, Vanderbilt University **INVITED**

Monolayer molybdenum disulfide (MoS2) is a two-dimensional crystal comprising a single layer of molybdenum atoms sandwiched between two layers of sulfur atoms. Monolayer MoS2 differs from its celebrated all-carbon cousin, graphene, by the presence of a direct band gap leading to robust light absorption and by strong electron-electron interactions leading to formation of rightly bound excitons. In this talk, we demonstrate that both electrical and optical properties of MoS2 can be widely tuned via external influences.

In the first part of the talk, we study changes in the bandgap and phonon spectra in strained MoS2. We investigate the transition from direct to indirect band gap in MoS2 under uniaxial strain. The experimental signatures of this transition include strain-induced changes in the PL wavelength and intensity.

Second, we examine the influence of the environment of MoS2 on its properties. We demonstrate substrate-induced scattering is suppressed in suspended MoS2 specimens. We use photocurrent spectroscopy to study excitons in pristine suspended MoS2. We observe band-edge and van Hove singularity excitons and estimate their binding energy. We study dissociation of these excitons and uncover the mechanism of their contribution to photoresponse of MoS2.

3:00pm **2D+AS+EM+MI+MN+NS+TF-WeA3 Electron-Phonon Coupling and Photoluminescence in Single Layer Transition Metal Dichalcogenides**, ***Neha Nayyar***, *V. Turkowski, D.T. Le, T.S. Rahman*, University of Central Florida

Single layer MoS$_2$ and other transition metal dichalcogenides have been the subject of numerous investigations because of their unusual optical, electronic and transport properties. To understand and thereby tune their photoluminescent properties, we have analyzed the role of electron-phonon interactions. Density functional perturbation theory is used to calculate the dispersion of system phonons, while electron-phonon coupling is obtained using the Eliashberg approach. Time-dependent density-functional theory based calculations using the density-matrix approach is employed to study the exciton and trion excitations which are found to appear as peaks in the absorption spectrum in the visible range with binding energy ~0.5 – 1 eV and ~0.02-0.03 eV, correspondingly. The emission peak is found to also lie in the visible spectrum and is sensitive to the value of the electron-phonon coupling, which depends on the nature and extent of doping. The position of the spectral peaks may thus be manipulated by doping. Calculations of the self-energy and spectral functions of doped systems show excitations to have 10-100 fs lifetime, which makes the system interesting for ultrafast applications. Comparison will be made of these optical properties of several single layer dichalcogenides and contact will be made with available experimental data. Work supported in part by DOE Grant No. DOE-DE-FG02-07ER46354

3:20pm **2D+AS+EM+MI+MN+NS+TF-WeA4 Temperature Dependent Photoluminescent Spectroscopy of MoS$_2$**, ***Michael Watson***, *J.R. Simpson*, Towson University & NIST, *R. Yan, H. Xing*, University of Notre Dame, *S. Bertolazzi, J. Brivio, A. Kis*, EPFL, Switzerland, *A.R. Hight-Walker*, NIST

We report temperature and power dependent photoluminescence (PL) of molybdenum disulphide (MoS$_2$). Mechanical exfoliation of MoS$_2$, from bulk provides single-layer flakes which are then transferred either to sapphire substrates or suspended over holes in Si/Si 3 N 4 . We measure temperature dependence from ≈ 100K to 400K and power dependence from ≈ 6μW to ≈ 7mW using an Argon laser at 514.5nm and a HeNe laser at 632.8 nm. The PL spectrum exhibits a main exitonic peak(A) at ≈ 1.87eV which consist of both neutral excitons and charged trions (A- or A+) [1]. The A exciton peak and the A- exciton peak redshift and broaden with increasing temperature and power. Along with the A peak, we observe a lower energy bound exciton (BE) that is likely related to defects. The BE,a broad peak centred at ≈ 1.7eV, linearly redshifts and narrows with increasing power. The power dependence of both the main and bound peak saturates above 0.5mW. Raman temperature and power dependence will also be discussed [2].

[1] KF. Mak et al. Nat. Mat 12,207(2013)

[2] R.Yan and J.R.Simpson, S. Bertolazzi and J. Brivio, M. Watson, X.Wu and A. Kis, T.Luo, H.G.Xing, A.R. Hight Walker, ACS Nano 8,1 (2013)

4:20pm **2D+AS+EM+MI+MN+NS+TF-WeA7 Effects of Dimensionality on the Raman and Photoluminescence Spectra of and TaSe$_2$ and TaS$_2$ Dichalcogenides**, ***Danilo Romero***, University of Maryland, College Park, *M. Watson, J.R. Simpson*, Towson University, *H. Berger*, Ecole Polytechnique Federale de Lausanne, Switzerland, *A.R. Hight Walker*, NIST

We investigate the effects dimensionality on the electronic properties through the optical spectra of the transition-metal dichalcogenides 2*H*-TaSe$_2$ and *1T*-TaSe$_2$, and 1*T*-TaS$_2$. In bulk, these materials exhibit electronic states from Mott insulator, commensurate and incommensurate charge-density phases, and superconducting ground state as function of temperature. We explore the evolution of these properties as the materials approach a few layers, achieved via mechanical exfoliation of bulk single-crystals. Raman and photoluminescence spectroscopy of 2*H*-TaSe$_2$ and *1T*-TaSe$_2$, and 1*T*-TaS$_2$, carried out over a wide-range of temperature, were used as a probe of the change of the electronic properties from the bulk to single-layer phases of the materials. Comparison of the phonon and excitonic transitions as a function of temperature and dimensionality will be presented.

4:40pm **2D+AS+EM+MI+MN+NS+TF-WeA8 Few-Layer and Symmetry-Breaking Effects on the Electrical Properties of Ordered CF$_3$Cl Phases on Graphene**, ***Josue Morales-Cifuentes***, *T.L. Einstein, Y. Wang, J. Reutt-Robey*, University of Maryland, College Park

An effective potential mechanism for breaking the inherent sublattice symmetry of graphene has been studied using DFT calculations on hexagonal boron nitride.[1] Electrical detection of CF3Cl phase transitions on graphene shows the existence of a commensurate ordered phase in which this can be tested.[2] We study the electronic properties of similar phases varying coverage and orientation of CF3Cl with respect of the graphene substrate using VASP ver 5.3.3, with ab initio van der Waals density functionals (vdW-DF1, vdW-DF2).[3] [4] Consistent with a physisorbed phase, binding energies are calculated to be on the order of 280meV, and insensitive to coverage and orientation of the CF3Cl molecules. Charge transfer was calculated to be sensitive with coverage, but not orientation, which is qualitatively consistent with experiment. For low coverages, sub-lattice symmetry breaking effects are responsible for gap openings in the order of 4meV, whereas for large coverages it is the formation of ordered overlayers that opens gaps of 15meV. Furthermore, in bilayer graphene at low coverage we estimate an enhanced gap of 20meV.

[1] Gianluca Giovannetti et al. , PRB **76**, 073103(2007)

[2] Yilin Wang et al. , APL **103**, 201606 (2013)

[3] Jiri Klimes et al. , PRB **83**, 195131 (2011)

[4] Kyuho Lee et al. , PRB **82**, 081101(R) (2010)

5:00pm **2D+AS+EM+MI+MN+NS+TF-WeA9 Optical Anisotropies in Layered Nanomaterials**, ***Jon Schuller***, UC Santa Barbara **INVITED**

In nanomaterials optical anisotropies reveal a fundamental relationship between structural and optical properties. In layered materials, optical anisotropies may result from in-plane and out-of-plane dipoles associated with intra- and inter-layer excitations respectively. In this talk, I describe a novel method wherein we resolve the orientation of luminescent excitons and isolate photoluminescence signatures from distinct intra- and inter-layer excitations, respectively. We compare photoluminescence anisotropies in materials with weak or strong interlayer coupling, MoS$_2$ and the organic semiconductor PTCDA respectively. We demonstrate that photoluminescence from MoS2 mono-, bi- and trilayers originates solely from in-plane excitons, whereas PTCDA supports distinct in-plane and out-of-plane exciton species with different spectra, dipole strengths and temporal dynamics. The insights provided by this work are important for understanding fundamental excitonic properties in layered nanomaterials and designing optical systems that efficiently excite and collectlight from exciton species with different orientations.

5:40pm **2D+AS+EM+MI+MN+NS+TF-WeA11 Mechanical Properties of 2D-Materials**, *J.M. Gonzales*, University of South Florida, *R. Perriot*, Los Alamos National Laboratory, ***Ivan Oleynik***, University of South Florida

Graphene and other two-dimensional (2D) materials possess extraordinary mechanical properties, which are currently being explored in various novel applications. Atomic force microscopy (AFM) nanoindentation experiments on both pristine and polycrystalline samples of 2D materials, while being successful in measuring overall mechanical performance of graphene, require some theoretical input to extract the important mechanical properties. Large-scale atomistic molecular dynamics simulations are used to predict the mechanical properties of 2D materials, such as the elastic moduli, breaking strength, stress/strain distributions, and mechanisms of fracture under conditions of AFM nanoindentation experiments. Perfect, defective, and polycrystalline samples are investigated using large-scale molecular dynamics simulations with a screened environment-dependent bond order (SED-REBO) potential. The mechanisms of crack propagation in both perfect and defective samples will also be presented.

6:00pm **2D+AS+EM+MI+MN+NS+TF-WeA12 Mechanical Control of Structural Phase Transitions in Two-Dimensional Mo- and W-Dichalcogenide Monolayers**, ***Evan Reed***, *K.-A.N. Duerloo, Y. Li*, Stanford University

Mo- and W- dichalcogenide compounds have a two-dimensional monolayer form that differs from graphene in an important respect: it can potentially have more than one crystal structure. Some of these monolayers exhibit tantalizing hints of a poorly understood structural metal-to-insulator transition with the possibility of long metastable lifetimes. If controllable, such a transition could bring an exciting new application space to monolayer materials beyond graphene. Here we discover that mechanical deformations provide a route to switching the thermodynamic stability between a semiconducting and a metallic crystal structure in these monolayer materials. We employ density functional and hybrid Hartree-Fock/density functional calculations including vibrational energy corrections to discover that single layer $MoTe_2$ is an excellent candidate phase change material. We identify a range from 0.3% to 3% for the tensile strains required to transform $MoTe_2$ under uniaxial conditions at room temperature. We elucidate the appropriate thermodynamic constraints for monolayers, which can differ from bulk materials. The potential for mechanical phase transitions is predicted for all six studied compounds. The potential application space ranges from catalysis to information storage and nanoscale electronics.

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

Practical Surface Analysis I
Moderator: Alexander Shard, National Physical Laboratory, Christopher Szakal, National Institute of Standards and Technology (NIST)

2:20pm **AS+BI+MC-WeA1 The Application of XPS to Study Corroded Stainless Steel Surfaces**, ***Helen Brannon***, *S.J. Coultas, J.D.P. Counsell, S.J. Hutton, A.J. Roberts, C.J. Blomfield,* Kratos Analytical Limited, UK*, J. Morrison*, The University of Birmingham, UK

The corrosion of structural materials in contact with hot, pressurised water, which is heavily dependent on the condition of the exposed surface, is a common problem in nuclear power processes. This side reaction is undesirable due to the reduced heat transfer efficiency which is caused by the deposited oxide layers.

X-ray photoelectron spectroscopy (XPS) is demonstrated as a quantitative surface analysis technique which can be used to determine the type of corrosion chemistry that occurs.

Stainless steel (316L) substrates containing 70% Fe, 18% Cr, 8% Ni and 2% Mo (as well as a low concentration of impurities) are suspended in water at 300 °C for 1000 hours. A metal oxide double layer is found to develop over time on the stainless steel surface: the top layer is a mix of magnetite (Fe_3O_4) and Nickel Ferrite ($NiFe_2O_4$) and the bottom layer is a mix of magnetite and chromite ($FeCr_2O_4$) (below is the base metal).

A high energy, medium sized argon gas cluster source is shown to be advantageous compared to a conventional monatomic argon ion source when depth profiling such layered structures, causing reduced structural and chemical damage from the ion beam sputtering process.

Data acquisition at small analysis areas gives well resolved spectra, revealing the multi-layered oxide structures produced from the corrosion process.

[1] Depth profiling of the Passive Layer on Stainless Steel using Photoelectron Spectroscopy, Wendy Fredrikkson, Uppsala University

[2] Applied Surface Science, 257, (2011), 2717–2730

[3] The Radiochemistry of Nuclear Power Plants with Light Water Reactors, By Kark-Heinz Neeb

2:40pm **AS+BI+MC-WeA2 Molecular Characterization of Lubricant Degradation Produced in a Tribological Wear Test Using TOF-SIMS and Scanned Microprobe XPS Imaging**, ***Gregory Fisher****, S.S. Alnabulsi,* Physical Electronics Inc.*, T. Le Monge,* Ecole Centrale de Lyon - LTDS, France*, J.S. Hammond*, Physical Electronics Inc.

Scanning Auger microscopy (SAM) and x-ray photoelectron spectroscopy (XPS) are today the most widely used surface analysis techniques for quantitative elemental and chemical analysis in tribology. Modern SAM instrumentation allows the elemental and chemical analysis of features at spatial resolutions down to 10 nm while modern scanning x-ray microprobe XPS instrumentation can provide even more complex chemical state surface characterization at a sub-10 µm spatial resolution. The use of a scanned x-ray microprobe enables chemical state imaging at a low x-ray fluence to minimize disturbance of the surface chemistry. Notwithstanding the aforesaid capabilities, the elucidation of molecular chemistry and lubricant degradation that occurs via tribological wear remains intractable by SAM and XPS analysis alone.

This study focuses on the application of time-of-flight SIMS (TOF-SIMS), with supporting XPS analysis for quantification, to determine the molecular decomposition and metal-organic reaction products of lubricants used in bio-diesel fuel. The test specimens were produced on a reciprocating cylinder-on-flat tribometer to simulate the piston / cylinder contact geometry and dynamics that are typical of internal combustion engines. The lubricant used in the bio-diesel fuel consists of C_{18} fatty acids at a concentration in the high part-per-million (ppm) range. The TRIFT mass spectrometer of the PHI *nanoTOF* provides an advantage for this study in that the wear track topography is effectively decoupled from the molecular characterization and imaging. The HR^2 imaging mode of the PHI *nanoTOF*, simultaneously achieving a spatial resolution < 400 nm and a mass resolution of $\approx$ 10,000 $m/\Delta m$, is an important asset in molecular identification and imaging.

3:00pm **AS+BI+MC-WeA3 Surfaces and Interfaces of Real-World Products: What Do We Really Need to Know and What Are The Best Ways to Find Out?**, ***Anna Belu***, *L. LaGoo, W. Theilacker*, Medtronic, Inc. **INVITED**

Real world components and products come in many shapes, sizes and materials, and their surface properties are critical for performance in many areas including adhesion, biocompatibility, corrosion, lubricity, and welding. Surface analysis tools are often employed to gain a fundamental understanding of surface properties of products in development, as well as to evaluate properties of surfaces and interfaces of products that are not performing as specified. This presentation will discuss best practices for analysis of real world samples in an industrial, mainly R&D, environment.

The culture of industry is typically fast paced with the goal being to get product into the hands of consumers as soon as possible. In this environment, the surface analyst is faced with the challenge of providing high quality information from a variety of materials and issues in a short amount of time. The requestor often wants a simple answer and is unaware that the analyst progresses through a series of questions such as What is the issue? What are the best tools to find the answer to the issue? Are the tools up to the task? Is the lab up to the task? What types of results are necessary? What types of samples are helpful? What is the most efficient way to obtain the data? Is it OK to use one tool and analyze one point on one sample? What are efficient ways to analyze data ? Do the results solve the problem? This presentation will discuss the consideration that goes into providing high quality data in a short amount of time and include several examples of surface analysis from real world products.

4:20pm **AS+BI+MC-WeA7 Forensic XPS Surface Characterization of Cosmetic Trace Evidence**, ***Brian Strohmeier***, Thermo Fisher Scientific*, R. Blackledge*, Independent Consultant

X-ray photoelectron spectroscopy (XPS) has a long distinguished history of providing important information on the surface chemistry of a wide variety of materials including: catalysts, ceramics, coatings, fibers, glass, metals, oxides, polymers, powders, semiconductors, thin films, and many others. In addition, studies involving the use of XPS have addressed numerous complex materials problems in a multitude of diverse fields such as: adhesion science, chemical surface treatments, corrosion, electronics, medical devices, oxidation, solar cells, and so on. Despite its many advantages and unique capabilities as a surface analytical technique, XPS has not been widely used in forensic science for the examination of specimens gathered at the scene of a crime. The main reasons for the lack of forensic studies involving XPS are: 1) the lack of standard forensic XPS methods and standard samples for comparison to real world samples; and 2) the historical long analysis times (hours per sample) and large analysis areas (several square millimeters) compared to other common forensic techniques such as Raman microscopy and scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM/EDS). Advances in XPS instrumentation over the last decade have now improved analysis times to minutes per sample and analysis areas down to the range of tens to hundreds of micrometers. Also, recently developed argon cluster ion sources now allow "soft" depth profiling of organic and polymeric species with minimal ion beam damage, thus preserving the chemical state information available from XPS. XPS, therefore, has increased potential for new forensic science applications involving the surface characterization of trace evidence materials. Previous work has demonstrated the potential of XPS for revealing unique surface chemical information for gunshot residue (GSR) and textile fibers. This presentation will describe the use of XPS for forensic characterization of cosmetic materials such as hair chalks, shimmer, and glitter. These types of cosmetic materials have a high probability of transfer and retention if a victim struggles with an assailant during an abduction or sexual assault and could help support an association between an assailant, a victim, and a specific crime scene in a specific case circumstance. XPS is an excellent technique for characterizing residues of these cosmetic materials.

4:40pm **AS+BI+MC-WeA8 Industrial Applications of Surface Analysis**, ***William Stickle***, *M.D. Johnson, G.A. DeHaan, J.A. Burgess*, Hewlett Packard

Using surface analysis has been a mainstay of industrial research and corporate analytical labs for more than thirty years. The applications of surface chemical analysis in an industrial setting range from the investigation of the composition and chemistry of buried interfaces of single molecule memory devices created in the R&D lab to the routine analysis of plasma treated polymer surfaces on the production line. Some analyses are performed to provide a 'yes' or 'no' answer to question such as 'Has the oxide been removed?' or 'Was the surface plasma treated?'. Other analyses are much more complicated and often require the application and correlation of several analytical methods. This correlation between techniques often occurs in the characterization of, for example, fab processes where a process may be characterized by x-ray photoelectron spectroscopy to understand the chemistry; but then the analysis needs to correlate to the information obtained by Auger electron spectroscopy or ToF SIMS which are the techniques of choice when the process is scaled to dimensions where XPS is not practical. Further, simple data processing, such as calculating atomic concentrations, is often not the end of the analytical story. Examples of using numerical methods such as linear least squares fitting or the application of Tougaard backgrounds to clarify an analysis will also be discussed. More detailed analyses can also be achieved by applying modeling methods such as SESSA or using simple overlayer models to describe a material. This presentation will cover these different aspects of surface chemical analysis in an industrial laboratory with practical examples of using XPS, AES and ToF SIMS for process characterization, materials development and failure analysis.

5:00pm **AS+BI+MC-WeA9 Peter Sherwood Mid-Career Award Talk: Chemical Analysis of Cells and Tissues with Imaging ToF-SIMS**, ***Lara J. Gamble***, *B. Bluestein, D. Graham*, University of Washington **INVITED**

The ability to image cells and tissues with chemical and molecular specificity could revolutionize our understanding of biological processes. It would increase our understanding of chemical changes in cells and tissues as a function of an applied stress or as a result of disease, and enable tracking the spatial distribution of metabolites and lipids. Chemistry of tumor microenvironments, lipid metabolomics relationship to cancer, delivery of nanoparticles to cells, and tissue repair could be visualized on a cellular and sub-cellular level. The sub-cellular resolution mass spectral imaging capability of ToF-SIMS holds the potential to achieve this possibility. ToF-SIMS analysis of biological samples from 2D images of tissue biopsies to 3D images of nanoparticles in cells will be presented including multivariate analysis of the ToF-SIMS image data. The ToF-SIMS images are also combined with optical images of the same samples (same slices and serial biopsy slices). This combination of images allows researchers to visualize a molecular map that correlates with specific biological features or functions. The potential to combine the ToF-SIMS images with other techniques will also be discussed.

5:40pm **AS+BI+MC-WeA11 Characterization Strategies for the Detection of Carbon Nanotubes within an Epoxy Matrix**, ***Justin Gorham***, *J. Woodcock, W.A. Osborn, J. Heddleston, K. Scott*, National Institute of Standards and Technology (NIST)

Carbon nanotubes (CNT) have been widely incorporated into composite systems due to the enhanced properties that they add to new and existing products, especially with respect to mechanical strength. X-ray photoelectron spectroscopy (XPS), in conjunction with SEM and Raman spectroscopy, has been employed in efforts to characterize several CNT: epoxy composite systems. This characterization approach was applied to composite systems with (1, 4 and 5) CNT weight percentages. Additionally, imaging XPS results will be presented to provide further insight into the dispersion quality on the micron scale. Challenges associated with overlapping spectral features, charging and a variety of other considerations regarding the surface and the bulk of the sample will be discussed.

6:00pm **AS+BI+MC-WeA12 Measuring Schmutz: Accounting for Adventitious Carbon Contamination in X-ray Absorption Spectra of Carbon-Based Materials**, ***Filippo Mangolini***, *J.B. McClimon, J. Hilbert, R.W. Carpick*, University of Pennsylvania

Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy is one of the most powerful weapons in the surface-analysis arsenal, since it provides insights into the local ordering, bonding configuration, oxidation state, and hybridization of the elements present in the near-surface region (information depth: ~5 nm). NEXAFS analyses are commonly performed under the assumption of chemical and structural homogeneity within the nanometer-depth scale probed. Unfortunately, this does not hold for the vast majority of solid surfaces due to the presence of complex surface and near-surface structures (*e.g.*, natural oxides, contamination) and can lead to large errors when analyzing elements that are simultaneously present in multiple layers. This is particularly challenging for carbon-containing materials previously exposed to air, as their carbon K-edge NEXAFS spectra are a convolution of the spectrum of the material under investigation and that of the adventitious carbon contamination. While analysis methods for determining the composition and thickness of each layer in a multilayer system without applying any destructive technique have been developed for X-ray photoelectron spectroscopy, no corresponding methodology has ever been reported for NEXAFS spectroscopy.

Here, we present a novel, non-destructive, and generally-applicable method for accounting for the contribution of thin overlayers (with thickness smaller than the information depth) from NEXAFS spectra of two-layered systems (constituted by a substrate covered by a surface layer) to give the corrected NEXAFS spectrum of the substrate. The new methodology is applied to NEXAFS data acquired on air-exposed hard carbon-based materials (ultrananocrystalline diamond and hydrogenated amorphous carbon) and allowed for the removal of the contribution of adventitious carbon contamination from the as-acquired spectra to give the intrinsic photo-absorption NEXAFS spectra of the materials under investigation. The results demonstrated that, in the case of amorphous carbon-based materials, significant errors, between 5% and 20%, could be introduced in the computation of the fraction of carbon atoms in different hybridization states if the contribution from the carbonaceous contamination layer is not removed from the as-acquired NEXAFS spectra. We also extract information about the composition and bonding found in the contamination layer.

The development of this novel methodology has important implications for the thorough investigation of the near-surface region of carbon materials as well as of the phenomena occurring in them in response to different energetic inputs (*e.g.*, temperature, mechanical stress).

Energy Frontiers Focus Topic
Room: 315 - Session EN+AS+EM-WeA

Organic-Inorganic Interfaces for Energy
Moderator: Ramana Chintalapalle, University of Texas at El Paso

2:20pm **EN+AS+EM-WeA1 Towards Efficient Solution Processed Organic Photovoltaic Devices**, ***Elsa Reichmanis***, Georgia Institute of Technology **INVITED**

Solution-processed π–conjugated semiconductors exhibit potential in the development of low-cost, light-weight and large-area flexible plastic optoelectronics, particularly photovoltaics (OPVs). However, one drawback to current OPVs is their limited efficiency. We have explored the use of donor-acceptor (D-A) hybridization to tailor HOMO/LUMO energy levels and thus the band gap. Materials exhibiting high charge carrier mobility and strong low-energy absorption profiles have been synthesized and characterized. Coupled with materials structure, the performance of devices fabricated using polymeric semiconductors depends critically upon alignment of the polymer chains at the nano- through meso- and macro-scales. Significant structure-process-property relationships that allow for enhancement of long-range order will be discussed. For instance, a lyotropic liquid crystalline (LC) phase has been observed in poly-(3-hexylthiophene) (P3HT) via solvent-evaporation induced self-assembly. The lessons learned through these studies may allow for simple, controllable, and cost-effective methodologies for achieving high performance flexible plastic electronic devices.

3:00pm **EN+AS+EM-WeA3 Understanding Carrier Dynamics in $Cu_2ZnSn(S,Se)_4$ Using Time-Resolved Terahertz Spectroscopy**, *G.W. Guglietta,* Drexel University*, K. Roy Choudhury, J.V. Caspar,* DuPont Central Research and Development*, **Jason Baxter***, Drexel University

We have used time-resolved terahertz spectroscopy (TRTS) to measure lifetimes and determine recombination mechanisms in $Cu_2ZnSn(S,Se)_4$ (CZTSSe) thin films fabricated from nanocrystal inks. TRTS probes photoconductivity on femtosecond to nanosecond time scales that are relevant for recombination in thin film photovoltaics. Terahertz frequencies (0.2-2.5 THz) correspond to typical scattering rates in semiconductors, enabling determination of carrier density and mobility. Ultrafast time resolution permits tracking the evolution of carrier density to determine recombination mechanisms. By manipulating the photoexcitation wavelength and fluence, we can tailor the generation profile of photoexcited carriers to distinguish between surface, Shockley-Read-Hall (SRH), and Auger recombination mechanisms and determine rate constants.

TRTS experiments and modeling were used to understand the role of recombination mechanisms and their contribution to CZTSSe photovoltaic performance. TRTS photoconductivity shows an instrument-limited onset within 1 ps of an ultrafast pump pulse, followed by a slow decay over nanoseconds. Photoconductivity decay kinetics were fit with a bi-exponential model with two time constants and a weight fraction. The short time constant is typically ~200 ps and roughly corresponds to diffusion to and recombination at the surface. The long time constant is typically ~2 ns and is attributed to SRH recombination. Assignment of these mechanisms is supported by the dependence of kinetics upon excitation fluence and wavelength. Normalized kinetics are independent of fluence over a range of 40x, indicating that no Auger recombination is occurring. Without Auger recombination, we can distinguish between surface and SRH rates by tuning the pump wavelength. As the excitation wavelength is shifted towards the blue, carriers are generated nearer to the front surface and the photoconductivity kinetics are sensitive to the surface recombination velocity. With blue excitation, we see that a larger fraction, ~0.5, of carriers recombine with a short time constant. With redder excitation wavelengths, the carriers are generated more evenly throughout the film and the kinetics are dominated by SRH recombination with the long time constant having a majority of the weight fraction, ~0.8. TRTS provides a pathway to determine performance-limiting recombination mechanisms and measure key parameters like SRH lifetime and surface recombination velocity, helping to direct the design of efficient thin film photovoltaics.

3:20pm **EN+AS+EM-WeA4 Comparative Study of the Doping Effects of Titanium and Nitrogen into Tungsten Oxide (WO_3) Thin Films for Photovoltaic Device Applications***, **Mirella Vargas**, C.V. Ramana*, The University of Texas at El Paso

Tungsten oxide (WO_3) is a technologically important n-type semi-conductor that is extensively studied in the fields of electronic and opto-electronic devices. Due to its unique properties such as a high work function and high-coloration efficiency, WO_3 is attractive for electrochromic and memory devices including large area information displays, smart-windows, and optical heat-mirrors. Low-dimensional structures of WO_3 coupled with an ideal band gap (E_g ~ 2.8 eV) have been employed as materials for the photocatalyst driven by visible light irradiation in dye-sensitized solar cells. In addition, WO_3 has also become a strong contender to replace indium-doped tin oxide or ITO thin films in transparent electrode applications. The present work is focused on WO_3 thin films characterized as promising transparent conducting oxide (TCO) materials by investigating doping effects on the structural, chemical, and optical properties. The incorporation of titanium (Ti) was achievable by depositing the films through co-sputtering of W and Ti metal targets. The sputtering powers to the W and Ti were kept constant at 100 W and 50 W, respectively, while varying the growth temperature (T_s) in the range of 25-500 ^{o}C. While all the samples are optically transparent, the structural quality of Ti-doped WO_3 films is dependent on T_s. Ti-doped WO_3 films grown at T_s<400 ^{o}C were amorphous. A temperature of 400 ^{o}C is critical to promote the structural order and formation of nanocrystalline films in the monoclinic phase. The optical constants and their dispersion profiles determined from spectroscopic ellipsometry indicate that there is no significant inter-diffusion at the film-substrate interface for W-Ti oxide film growth of ~40 nm. The index refraction (*n*) at l=550 nm vary in the range of 2.15-2.40 with a gradual increase in growth temperature. Nitrogen (N_2) incorporation was made through a post-deposition anneal in an ammonia environment on WO_3 films. The un-doped WO_3 films grown by variable growth temperature will be annealed at high temperatures for various rates to accommodate a strong N_2 incorporation. The tungsten oxynitride films will be characterized by various analytical techniques to compare the doping effects of Ti and N_2 on the structural, electronic, and optical properties of WO_3 thin films.

5:00pm **EN+AS+EM-WeA9 Engineering Exciton Recombination in Organic Light-Emitting Devices***, **Russell Holmes***, University of Minnesota **INVITED**

While capable of realizing very high peak efficiency, many organic light-emitting devices (OLEDs) suffer a significant reduction in efficiency under large injected current densities. This efficiency roll-off can limit device brightness and potentially compromise operational stability. Much previous work has identified the key contributing factors to the efficiency roll-off in phosphorescent OLEDs as triplet-triplet annihilation and triplet-polaron quenching. Here, the parameters associated with these quenching processes are independently measured, and the impact of the exciton recombination zone width on the quenching processes in various OLED architectures is examined directly. In high efficiency devices employing a graded-emissive layer (G-EML) architecture the roll-off is due to both triplet-triplet annihilation and triplet-polaron quenching, while in devices which employ a double-emissive layer (D-EML) architecture, the roll-off is dominated by triplet-triplet annihilation. Overall, the roll-off in G-EML devices is found to be much less severe than in the D-EML device. This result is well accounted for by the larger exciton recombination zone that is experimentally measured in G-EML devices, serving to reduce exciton density-driven loss pathways. Indeed, a predictive model of the device efficiency based on the quantitatively measured quenching parameters shows the role a large exciton recombination zone plays in mitigating the roll-off.

5:40pm **EN+AS+EM-WeA11 Interface Engineering to Control Magnetic Field Effects of Organic-based Devices by using a Self-Assembled Monolayer***, **Hyuk-Jae Jang**,* NIST & WFU*, S.J. Pookpanratana,* NIST*, A.N. Brigeman,* Wake Forest University*, R.J. Kline,* NIST*, J.I. Basham,* NIST & PSU*, D.J. Gundlach, C.A. Hacker, O.A. Kirillova,* NIST*, O.D. Jurchescu,* Wake Forest University*, C.A. Richter*, NIST

Magnetic field effects (MFEs) in non-magnetic organic semiconductors provide a non-contact approach to control electronic and optoelectronic properties of organic-based devices by using a sub-tesla magnetic field and thus they have been of great interest to industry as well as academia around the world.[1,2] However, there is no consensus on the physical mechanism(s) causing the MFEs in organic semiconductors even though a variety of fundamental models have been proposed to explain the effects.[2] Studies on many different organic semiconductors and organic-based structures have shown that the magnitude and even the sign of the MFEs can vary by changing the measurement and fabrication conditions such as bias voltage, film thickness, and temperature. Therefore, it is suggested that there can be multiple origins inducing the MFEs and the outcome may result from a competition between different MFE mechanisms.[2]

In this presentation, we report a novel method of manipulating the MFEs on electrical resistance of organic semiconductors, namely organic magnetoresistance in Alq_3 (tris-(8-hydroxyquinoline) aluminum) – based devices by simply adding a molecular self-assembled monolayer (SAM) between a metal electrode and an organic semiconductor. SAMs have been known for their versatile use in various technological applications.[3] Particularly, SAMs can alter the physical property of an inorganic solid surface and thus modify the interface between an electrode and an organic thin film when a SAM is inserted between them.[3] We show for the first time that the interfacial modification by simply inserting a fluorinated SAM (heptadecafluoro-1-decanethiol $[CF_3(CF_2)_7(CH_2)_2SH]$ or F-SAM) in organic-based devices changes the sign of organic magnetoresistance due to the change in relative strength of different MFE mechanisms coexisting in organic-based devices. In addition, we utilize different MFE mechanisms coexisting in organic-based devices by adding a thin TPD (N,N′-Bis(3-methylphenyl)-N,N′-diphenylbenzidine) layer to create a system whose organic magnetoresistance can be tuned by an external bias voltage.

References

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6:00pm **EN+AS+EM-WeA12 Study on the Correlation between Electrode-Active Layer Interfaces and Performance of Polymer Solar Cells***, **Huanxin Ju**, J.F. Zhu*, University of Science and Technology of China

The PSCs were fabricated with different cathodes (Ca/Al and Al) as the electron-collection layers and with PCDTBT (poly[N-9”-hepta-decanyl-2,7-carbazole-alt-5,5-(4’,7’-di-2-thienyl-2’,1’,3’-benzothiadiazole)]) and PC70BM ([6,6]-phenyl-C71-butyric acid methyl ester) as the active layers.

The Ca/Al interlayer significantly improves the open circuit voltage (VOC), short circuit current (JSC), fill factor (FF) so as to improve the PCE in comparison with Al as the cathode. In order to understand how the electrodes affect the device performance, the Ca/PCDTBT and Al/PCDTBT interfaces were investigated by transient photovoltage (TPV), charge extraction (CE) and synchrotron radiation photoemission spectroscopy (SRPES). The TPV and CE measurements were used to determine the charge carrier lifetime and density. Charge carrier recombination rate constant was found to be much smaller in the device with Ca/Al cathode as compared to that with Al cathode. Energy band diagrams and interfacial chemical reactions were characterized using high-resolution SRPES. The results indicate that the Ca interlayer can induce the stronger dipole moment, which facilitates electrons collection and drives holes away at the cathode/polymer interface. The device performance was improved because of the lower recombination.

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

Nanoscale Imaging and Materials Characterization

Moderator: Craig Prater, Anasys Instruments, Paul Sheehan, Naval Research Laboratory

2:20pm **NS+AS-WeA1 2014 AVS Albert Nerken Mark Award Lecture - Brilliant Nanodiamond Particles**, ***Olga Shenderova****, Adámas Nanotechnologies Inc., *G.E. McGuire*, International Technology Center **INVITED**

Despite that nanodiamond (ND) particles were discovered more than 50 years ago and were mass produced in the early 80s, for a long time they were in the shadow of their more famous sp^2 carbon cousins. Two recent major breakthroughs, production of individual 4-5nm particles and particles containing colour centres exhibiting stable luminescence and unique spin properties have brought ND particles to the forefront of materials research.[1] Nanometer size particles are produced by detonation of carbon-containing explosives or by grinding of microdiamond powders. Besides well-known outstanding mechanical and thermal properties, diamond particles have remarkable optical properties in combination with biocompatibility, high specific surface area, and tuneable surface structure. Applications of ND which have captivated the imagination of scientist in areas which have broad societal impact, such as energy preservation and biomedical imaging, will be briefly illustrated and a more in-depth review of their optical properties provided.

The optical emission, scattering and attenuation of ND are finding unique applications. In life sciences nanoparticles are increasingly used as fluorescent probes to monitor cellular interactions and study cellular dynamics at the single molecular level. Foreign atoms can be incorporated into the lattice of ND particles providing photostable particles as well as systems for quantum sensing that may be used to probe the intracellular environment at the nanoscale. Development of multimodal imaging probes based on 5-10nm ND and doping of ND with different elements to generate photoluminescence at alternative wavelengths are future directions for this field. Carbon dot-decorated ND is another means of generating photoluminescent nanoparticles with tuneable emission over the visible to near-infrared portion of the electromagnetic spectrum. The photoluminescent ND is increasingly being viewed as a means of drug delivery. Encapsulating ND in a porous silica shell is a means of achieving stable fluorescent imaging with nanoparticles with a high loading capacity for bioactive molecules.

Due to its high refractive index, wide bandgap and crystalline lattice, ND highly attenuates and scatters ultraviolet radiation. High attenuation and scattering in combination with large surface area has been shown as a means of increasing the radiation resistance of polymer nanocomposites. This can be beneficial in sunscreens as well as in polymers used in the construction of satellites to be placed in low Earth orbit.

[1] V.Mochalin, O.Shenderova, D.Ho and Y.Gogotsi, “The properties and applications of nanodiamonds”, (2012) *Nature Nanotechnology*, 7 (1) 11-23.

3:00pm **NS+AS-WeA3 Oxidation State Sensitive Imaging of Ceria Nanoparticles**, ***Aaron Johnston-Peck***, National Institute of Standards and Technology (NIST)

Scanning transmission electron microscopy (STEM) coupled with electron energy loss spectroscopy (EELS) has been successfully applied to track changes to composition as well as bonding environment with atomic resolution. These measurements impose exacting experimental and instrumentation requirements that include aberration-corrected optics, electron sources with narrow energy spreads, and extremely stable room environments. Therefore it seems prudent when possible that other techniques with less demanding experimental requirements supplement EELS measurements. Imaging or diffraction techniques greatly relax these aforementioned requirements as the need for corrective optics and narrow energy spreads can be eliminated. Moreover the possibility of beam induced artifacts is reduced because the total electron dose needed to form an image or diffraction pattern is less than an EELS spectrum image.

Low angle annular dark field (LAADF) STEM is presented as an alternative to EELS measurements to identify changes to local changes of oxidation state in ceria (CeO_2) nanoparticles. This relationship was established through the use of EELS, *in-situ* measurements, and image simulations. Ceria has numerous energy related applications due to the ability of ceria readily store and release oxygen. The formal charge of the cerium ions transition from 4+ to 3+ as oxygen vacancies are formed. These oxygen vacancies cause local distortions to the crystal and subsequently produces additional diffuse scattering to low angles. The LAADF STEM signal is sensitive to this change in scattering and contrast variations in the image become resolved. Additionally, preliminary experiments on other metal oxide nanoparticles suggest that this approach may be applied to other material systems and processes as well.

3:20pm **NS+AS-WeA4 Shape and support interaction of size-selected Pd and Pt NPs on $TiO_2(110)$**, ***Mahdi Ahmadi***, *F. Behafarid*, University of Central Florida, *B. Roldan Cuenya*, Ruhr-University Bochum, Germany

The shape and the support interaction of 3D palladium and platinum nanoparticles (NPs) deposited on $TiO_2(110)$ was investigated using scanning tunneling microscopy (STM). The NPs were synthesized using inverse micelle encapsulation. In spite of the initial random location of the micelle-prepared NPs on the support, step edge decoration was observed after annealing at high temperature (>1000°C). In general, resolving the shape of 3D NPs using STM is very challenging due to the tip-convolution effects. However, a combination of ultra-sharp STM tips and samples containing structurally well-defined NPs allowed us to resolve the NP shape, with the highest features on the NPs being unaffected by tip artifacts. It was found that all NPs had a truncated octahedron shape, with {111} top and interfacial facets. Furthermore, the alignment of the NP edges (or symmetry axes) with the $TiO_2(110)$-[001] atomic rows evidenced the epitaxial relationship with support achieved after annealing. The STM data were analyzed following the Wulff-Kaischew theorem, and a MATLAB code was used to reconstruct the NP shape, eliminating overestimations in the lateral size inherent to the STM technique due to tip effects. The surface energy ratio $\gamma_{100}/\gamma_{111}$ was calculated for each Pd NP with an average value of 1.12±0.07, which is in good agreement with theoretical values. Moreover, the adhesion energy was found to display a size-dependence, with larger NPs having smaller adhesion energy. This phenomenon can be explained based on the minimization of the interfacial strain by reducing the contact area. Following similar analysis of Pt NPs on $TiO_2(110)$, a higher $\gamma_{100}/\gamma_{111}$ ratio of 1.18±0.1 was obtained as compared to Pd. Also, the rate of decrease in the adhesion energy with increasing NP height was lower for Pt as compared to Pd.

4:20pm **NS+AS-WeA7 Nanoscale Imaging and Spectroscopy of Plasmonic Hot Spots and Dark Modes with the PTIR Technique**, ***Andrea Centrone***, National Institute of Standards and Technology (NIST) **INVITED**

Localized surface plasmon resonances couple propagating light with nanoscale volumes of matter (hot-spots), enabling new applications in sensing and therapeutics. Surface-Enhanced Infrared Absorption (SEIRA) Spectroscopy exploits such hot-spots for sensitive chemical detection. Calculations predict large SEIRA enhancement factors but the diffraction of long IR wavelengths (2 µm - 16 µm) has hindered the experimental determination of SEIRA enhancements with nanoscale resolution.

Photo Thermal Induced Resonance (PTIR) combines the chemical specificity of IR spectroscopy with the lateral resolution of Atomic Force Microscopy (AFM). PTIR circumvents the limitations of light diffraction by employing an AFM tip as a local detector for measuring the transient thermal expansion induced by the absorption of light pulses in the sample. Local IR spectra and composition maps are obtained recording the amplitude of the tip deflection as a function of the laser wavelength and position, respectively. Notably, the PTIR signal is proportional to the absorbed energy (not scattering) and the PTIR spectra are directly comparable with IR spectral libraries, enabling materials identification.

In this work, the PTIR technique is applied to image the dark plasmonic resonance of gold Asymmetric Split Ring Resonators (A-SRRs) in the mid-IR with nanoscale resolution. Additionally, the chemically-specific PTIR

*** Albert Nerken Award Winner**

signal is used to map the local absorption enhancement of PMMA coated A-SRRs, revealing hot-spots in the resonators' gaps with enhancement factors up to ≈ 30.

The local information gathered with in the PTIR experiments can provide insightful information and possibly help to engineer nanomaterials for greatest efficacy. As an additional example the PTIR technique will be applied to image phase separated domains in Metal-Organic Frameworks single crystals, a novel class of materials that find application in catalysis, sensing and separation.

5:00pm **NS+AS-WeA9 AFM-based Infrared Spectroscopy—Nanoscale Chemical Analysis with Sensitivity Down to Single Monolayers**, ***Craig Prater***, *K. Kjoller, M. Lo, E. Dillon, R. Shetty,* Anasys Instruments, *C. Marcott,* Light Light Solutions, *F. Lu, M. Jin, M. Belkin,* University of Texas at Austin, *A. Dazzi*, Université Paris-Sud, France

The ability to perform chemical analysis at the nanoscale has been considered one of the "holy grails" of the scanning probe microscope community. Many techniques have been developed to provide material contrast in SPM images based on a variety of properties (electronic, optical, mechanical, etc.), but there had not been the ability to perform broadly applicable chemical analysis on diverse samples. We have developed AFM-based infrared spectroscopy (AFM-IR)[1] that enables broadly applicable chemical analysis on samples with nanoscale spatial resolution and with sensitivity down to the scale of individual molecular monolayers. The AFM-IR technique illuminates a sample with light from a tunable infrared laser source and then uses the tip of an AFM to measure the sample's local photothermal expansion due to the absorption of infrared light at specific wavelengths.[2] Measuring absorption as a function of wavelength creates an IR absorption spectrum that acts as a chemical fingerprint to characterize and identify chemical components. Mapping IR absorption spatially over a sample at different wavelengths can be used to create maps of nanoscale chemical composition. Recently we have implemented two techniques to extend both the applicability and sensitivity of the AFM-IR technique. First, we implemented top side illumination to enable AFM-IR on a much wider array of samples and sample substrates. Second, we developed a resonance enhanced mode[3] where the IR laser pulses are synchronized to a contact resonance of the AFM cantilever. Combined with "lightning rod" enhancement of the incident IR light, the resonance enhanced technique can achieve chemical analysis with single monolayer sensitivity[4] and spatial resolution ~25 nm. We will describe the AFM-IR technique, recent innovations and applications in materials, life sciences, photonics, and semiconductors.

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5:20pm **NS+AS-WeA10 Schottky Barrier Height Mapping of Nanoengineered Metal/Semiconductor Interfaces**, ***Robert Balsano***, *C. Durcan,* University of Albany-SUNY, *A. Matsubayashi, V.P. LaBella*, University at Albany-SUNY

Metal/semiconductor junctions form rectifying contacts known as Schottky diodes, which have an energy barrier determined by charge transfer and bonding at the interface. Current-voltage and capacitance-voltage spectroscopy measurements yield a spatially averaged barrier height. Ballistic electron emission microscopy (BEEM) is a scanning tunneling microscopy (STM) technique that can measure transport of hot electrons through materials and interfaces locally with high spatial and energetic resolution due to the precise positioning of the STM tip. This presentation details work done to map the Schottky barrier height with nanoscale resolution at several metal/semiconductor interfaces. These maps can give insight into the homogeneity of the barrier height as well as the spatial distribution of individual metal species. Potentially this technique can be used to image nanoengineered interfaces.

5:40pm **NS+AS-WeA11 Scanning Electron Microscopy to Probe Electron Transport of Working Nanodevices under Realistic Operation Conditions**, ***Ana Stevanovic***, *A. Kolmakov*, National Institute of Standards and Technology (NIST)

The interplay between the electron transport and chemical status of the surface of working nanodevices can be affected by local electroactive inhomogeneities (defects), presence of near surface depletion regions and Schottky contacts. In spite of tremendous progress achieved in understanding of semiconductor chemical sensors, very little experimental data are available on aforementioned interplay in working devices under realistic operation conditions. Ambient pressure electron microscopy is used in this work to address *in situ* imaging of a formation of electroactive inhomogeneities inside a model SnO_2 nanowire device as a function of gas environment and temperature under realistic operating conditions. In addition, using scanning photoelectron and Auger microscopy with the lateral resolution of ca 80 nm, we are able to access spectroscopically the fine changes in surface condition of an individual SnO_2 nanowire during their operation. It is possible to monitor the changes in a conductance of the SnO_2 nanodevice in operando mode upon exposures to different redox gases and relate them to the formation of the specific surface groups.

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.

References

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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.

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 $< 15\ \mu s$.[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_2O_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_2O_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_2O_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.

Helium Ion Microscopy Focus Topic
Room: 316 - Session HI+2D+AS+BI+MC-ThM

Fundamental Aspects and Imaging with the Ion Microscope

Moderator: Gregor Hlawacek, Helmholtz-Zentrum Dresden - Rossendorf, Stuart Boden, University of Southampton

8:00am **HI+2D+AS+BI+MC-ThM1 He+ and Ne+ Ion Beam Microscopy and Microanalysis**, ***David C. Joy***, University of Tennessee, Oak Ridge National Laboratory **INVITED**

After one hundred years of use the electron microscope is now being overtaken by ion beam systems because of their many advantages. A wide variety of different ions are available, each of which has its own particular strengths, but the two most commonly used at present are Helium (He+) and Neon (Ne+). Changing from one to the other takes only a couple of minutes to complete. for operation at beam energies between 20 and 50kV both He+ and Ne+ generate 'ion induced secondary electrons' (iSE) which yield images which are comparable with those from a conventional SEM but offer image resolutions of 0.4nm or less even on bulk samples, a much greater depth of field, and an enhanced signal to noise ratio. At typical imaging currents between 10-12 to 10-14Amps damage to most samples is very limited for He+ although more severe for Ne+ but at higher beam currents both He+ and Ne+ can pattern, deposit, or remove, a wide range of materials. In such applications He+ provides the best resolution, but Ne+ is much faster.

The production of X-rays depends on the speed of the incident particle, not on its energy. At typical operating energies the He+ or Ne+ ions are traveling too slowly to generate X-rays so another approach is required for chemical microanalysis. The most promising option is "Time of Flight-Secondary Ion Mass Spectrometry" (TOF-SIMS). Here the incoming ion "splashes" material from the top few layers of the specimen surface. These fragments are then characterized by determining their mass to charge ratios. The chemical data this generates is much more detailed than the bare list of elements that is produced by X-ray microanalysis.

8:40am **HI+2D+AS+BI+MC-ThM3 Gas Field Ion Sources**, ***Jason Pitters***, *R. Urban,* National Institute for Nanotechnology, Canada*, R. Wolkow*, University of Alberta and The National Institute for Nanotechnology, Canada **INVITED**

Single atom tips (SATs) prepared by the spatially controlled field assisted etching method are proving to have utility as ion sources, electron sources and in scan probe applications.

As Gas Field Ion Sources (GFISs), there is potential for operation in scanning ion microscopes (SIMs) and our efforts to prepare and characterize SAT ion emission will be discussed. It will be shown that etching to a single atom tip occurs through a symmetric structure and leads to a predictable last atom. SATs can be prepared reproducibly with emission along a fixed direction for all tip rebuilds. It will also be shown that the emission properties of the SAT can be altered by shaping of the tip shank during the etching procedure. In this manner, the operating voltage can be controlled and a lensing effect of the tip base is demonstrated. During formation, the tip shape can be evaluated by using both helium and neon imaging gases. The stability of helium and neon ion beams generated by SATs will also be demonstrated and compared to other tip orientations. The remarkable robustness of these tips to atmosphere exposure will also be shown and the ability to prepare SATs from material other than tungsten will be demonstrated.

SATs also have utility in electron emission. By shaping the tip appropriately, electron emission characteristics can also be tailored and the coherence properties of an SAT will be presented as deduced from holographic measurements in a low-energy electron point source microscope. Initial utility in scan probe experiments including atomic force microscopy and scanning tunneling microscopy will also be discussed.

9:20am **HI+2D+AS+BI+MC-ThM5 Ion Beam Profiles Generated by W(111) Single Atom Tips**, ***Radovan Urban***, *R. Wolkow,* University of Alberta and The National Institute for Nanotechnology, Canada*, J.L. Pitters*, National Institute for Nanotechnology, Canada

Single atom tips (SATs) gained significant attention over the past decade because they serve as high brightness, field emission electron sources and gas field ion sources (GFISs). Small virtual source size makes these attractive candidates for advanced scanning imaging applications such as SEM, TEM, and scanning ion microscopy (SIM) as well as for non-staining ion beam writing applications.

The ion beam diameter σ, together with total ion current I generated by a single surface atom of W(111) nanotip, are crucial parameters which determine angular current density and brightness of gas field ion sources. It is, therefore, essential to understand underlying mechanisms that govern beam width. Furthermore, mapping both σ and I to a large parameter space of tip temperature, imaging gas pressure, and extraction voltage is necessary to optimize gas field ion source operation. In this contributions we will explore both σ and I as a function of temperature and extraction voltage at different imaging gas pressures using a field ion microscope (FIM) to monitor beam shape and total current. The qualitative model of our results will be also discussed. Finding "the best imaging voltage" for a SAT will be briefly discussed.

9:40am **HI+2D+AS+BI+MC-ThM6 Defect Observation by using Scanning Helium Ion Microscopy**, ***Hongxuan Guo****, L. Zhang, D. Fujita*, National Institute for Materials Science (NIMS), Japan

Scanning helium ion microscopy (HIM) is an innovative method to characterize surface of various materials. With a secondary electron detector (SED) and a micro plate detector (CPD), Orion Plus system can obtain surface information including morphology , composition, and crystal orientation. [1, 2] Improve the abilities of characterization of materials with HIM will benefit the develop of new materials, such as structure materials including metals, ceramics and others.

In this presentation, we will show the investigation of the crystal structure of metal with HIM. We prepared an sample stage with a reflector that can be used to obtain the transmission helium ions intensities in the samples. With this sample stage, we observed the Ni-Co base super alloy and aerogel composed with hollow nanosphere. The Rutherford backscattered image (RBI) of metal surface show different orientation of poly crystal. The nano-twins and other defects in Ni-Co base superalloy were investigated by HIM in scanning and transmission mode. The nano-twins also be observed by other techniques, such as transmission electron microscopy and electron backscatter diffraction. The scattering of helium ions with different energy was analyzed. This work provide some new methods to improve the research on defects and structure of crystal.

[1]. H. X. Guo, D. Fujita, Scanning helium ion microscopy, Characterization of Materials, 2nd Edition(Wiley, New York, 2012)

[2]. H. X. Guo. J. H. Gao, M. S. Xu, D. Fujita, Applied Physics Letters, 104, 031607 , 2014

11:00am **HI+2D+AS+BI+MC-ThM10 Helium Ion Microscopy (HIM) for the Imaging of Biological Samples at Sub-nanometer Resolution**, ***James Fitzpatrick***, Salk Institute for Biological Studies **INVITED**

Scanning Electron Microscopy (SEM) has long been the standard in imaging the sub-micrometer surface ultrastructure of both hard and soft materials. In the case of biological samples, it has provided great insights into their physical architecture. However, three of the fundamental challenges in the SEM imaging of soft materials are that of limited imaging resolution at high magnification, charging caused by the insulating properties of most biological samples and the loss of subtle surface features by heavy metal coating. These challenges have recently been overcome with the development of the Helium Ion Microscope (HIM), which boasts advances in charge reduction, minimized sample damage, high surface contrast without the need for metal coating, increased depth of field, and 5 angstrom imaging resolution. We demonstrate the advantages of HIM for imaging biological surfaces as well as compare and contrast the effects of sample preparation techniques and their consequences on sub-nanometer ultrastructure.

11:40am **HI+2D+AS+BI+MC-ThM12 Helium Ion Microscopy of Biological Cells**, ***Natalie Frese****, A. Beyer, M. Schürmann, B. Kaltschmidt, C. Kaltschmidt, A. Gölzhäuser*, University of Bielefeld, Germany

In this presentation HIM images of biological cells are presented. The presented study focuses on neuronal differentiated human inferior turbinate stem cells, mouse neurons and mouse fibroblasts. The cells were prepared by critical point drying or freeze drying and a flood gun was used to compensate charging, so no conductive coating was necessary.

Therewith, extremely small features at native cell surfaces were imaged with an estimated edge resolution of 1.5 nm. Due to the size of the structures and the preparation methods of the cells the observed features could be an indicator for lipid rafts. This hypothesis will be discussed.

12:00pm **HI+2D+AS+BI+MC-ThM13 Helium Ion Microscopy Analysis of Ag Nanoparticle Implanted Biological Samples for MILDI-MS (Matrix Implanted Laser Desorption/Ionization) Imaging***, S. Shubeita,* Rutgers University*, L. Muller,* NIDA-IRP*, H.D. Lee, C. Xu,* Rutgers University*, D. Barbacci,* Ionwerks Inc.*, K. Baldwin,* NIDA-IRP*, J.A. Schultz,* Ionwerks Inc.*, L. Wielunski,* ***Torgny Gustafsson****, L.C. Feldman,* Rutgers University*, A.S. Woods*, NIDA-IRP

MILDI mass spectrometry is an emerging tool for detecting changes in brain tissue. An ~20 nm thick region of rat brain tissue implanted with 10^{13}/cm^2 Au$_{(400)}^{4+}$ nanoparticle (NP) ions at 40 keV, produces analytically useful signals of lipids, peptides and proteins using a pulsed nitrogen laser [1]. When a dose of 10^{12}/cm^2 500 eV AgNP (approximately 6 nm diameter) is implanted as a matrix, only lipids are detected [2]. To understand this it is essential to measure the spatial distribution of the nanoparticles. We have used Rutherford Backscattering and Helium Ion Microscopy imaging to determine the Ag NP distributions and areal densities in an implanted coronal rat brain section. We then correlate the ion beam analysis and imaging with individual lipid intensities from several hundred MILDI mass distributions. The results show a high degree of uniformity of the Ag atomic and particulate distribution on a sub-micron scale among different regions of the tissue. Helium Ion Microscopy provides verification of NP matrix uniformity, validating the use of MILDI for quantitative mass analysis.

This work is partially supported by NSF (DMR 1126468), NIH (R44DA030853-03) and IAMDN.

[1] A. Novikov et al, *Analytical Chemistry* 76 (2004) 7288. [2] S. N. Jackson et al, *Analyt. and Bioanal. Chem.* (e-pubed Dec 2013).

Fundamentals & Biological, Energy and Environmental Applications of Quartz Crystal Microbalance Focus Topic
Room: 317 - Session QC+AS+BI+MN-ThM

Fundamentals and Method Development of QCM
Moderator: Ralf Richter, CIC biomaGUNE & MPI for Intelligent Systems, W.K. Hiebert, University of Alberta and The National Institute for Nanotechnology

8:40am **QC+AS+BI+MN-ThM3 High-Frequency Contact Mechanics Studies with a QCM**, ***Diethelm Johannsmann***, Clausthal University of Technology, Germany **INVITED**

Studying particulate objects with a QCM is challenging with regard to interpretation, but also of outstanding interest. Potential samples would be (bio-) colloids, vesicles, granular matter, bacteria or technical multi-contact interfaces. The analysis must build on the small-load approximation, which states that the shifts in resonance frequency and resonance bandwidth are proportional to the in-phase and the out-of-phase component of the area-averaged stress at resonator surface. For realistic modeling, a numerical code is needed which predicts this stress field from the geometry and all materials parameters involved. There is such a model in two dimensions, building the finite element method.

On a simpler level, the behavior of particles on a resonator surface can also be understood from the coupled resonance model. The particles in contact form small resonators of their own, where the "particle resonance frequency" is determined by the mass and the stiffness of the contact. If the particle resonance frequency in the range of frequencies amenable to the QCM one observes a coupled resonance, meaning that the shifts of resonance frequency and resonance bandwidth themselves form a resonance curve when plotted versus overtone order. Depending on whether the particle resonance frequency is higher or lower than the QCM frequency, the frequency shift can be positive or negative. From the particle resonance frequency, one can assess the stiffness of the contact between the particle and the surface.

The detailed investigation of the coupled resonance picture reveals a problem. though. FEM models of the corresponding geometries reveal two coupled resonance, occurring at different frequencies. They corresponding to a rotation of the particle about the point of contact (the "rocking mode") and a rotation about the center of mass (the rotational mode"). The problem complicates the interpretation of experimental data, but it points to an intriguing analogy between QCM experiments a vibrational spectroscopy. A QCM experiment amounts to a vibrational spectroscopy on surface-attached colloids.

The last part of the talk is concerned with a novel sensing dimension of the QCM, which is the dependence of frequency and bandwidth on amplitude. Such dependences are ubiquitous in contact mechanics experiments and can be understood in terms of partial slip. The contacts behave nonlinearly. Nonlinear behavior can also be observed in liquids, where it is caused by the nonlinear term in the Navier-Stokes equation. The nonlinear term drives a steady flow of liquid along the direction of oscillation towards the center of the plate.

9:20am **QC+AS+BI+MN-ThM5 Study of Water Adsorption and Capillary Bridge Formation for SiO_2 Nanoparticle Layers by Means of a Combined *In Situ* FT-IR Reflection Spectroscopy – QCM-D Set-up**, ***Boray Torun***, *C. Kunze,* University of Paderborn, Germany*, C. Zhang, T.D. Kühne,* Johannes Gutenberg University Mainz, Germany*, G. Grundmeier*, University of Paderborn, Germany

During the past decade nanoparticles attracted a great deal of attention and found many applications in various fields ranging from pigments and antibacterial agents to highly effective catalysts. In this context, the handling and processing of nanoparticle powders play an important role. In contrast to macroscopic particles, nanoparticle flow properties are manly governed by the particle-particle interactions. The forces determining these interactions strongly vary not only with the material properties but also with surface chemical composition as well as the environmental conditions. Hence, a fundamental understanding of the processes and forces involved plays a key role for the prediction of nanoparticle powder behavior.

In the presented study [1], water adsorption and capillary bridge formation within a defined layer of SiO_2 nanoparticles was studied by means of a novel *in-situ* analytical setup allowing for combined quartz crystal microbalance with dissipation analysis (QCM-D) and Fourier transformation infrared reflection absorption spectroscopy (FT-IRRAS). On the one hand, the QCM-D gave insights on both, mass change (Δf) and changes in the contact mechanics, indicated by dissipation changes (ΔΓ), whereas on the other hand FT-IRRAS allowed for the characterization of the adsorbed water structure. Employing peak deconvolution to the OH-signal in the region of 3400 cm^{-1}, "ice-like" and "liquid-like" water structures could be clearly identified.

Combined measurements show that for a monolayer of monodisperse SiO_2 particles with a diameter of about 250 nm the adsorption of water leads to a linear increase in dissipation for relative humidity (RH) values up to 60%. Subsequently, the strong increase in dissipation between 60% and 80% RH was attributed to the actual liquid bridge formation. This result was supported by the predominant growth of "liquid-like" water during the bridge formation phase indicated by the corresponding FT-IR data. Furthermore, for RH>90% a decrease in dissipation was detected indicating the merging of capillaries and the onset of a water film formation. Overall, our results indicate that combined in-situ QCM-D and FT-IRRAS analysis enables the qualitative and quantitative analysis of water adsorption and capillary bridge formation in particle layers.

[1] Torun, B. et al., *Phys. Chem. Chem. Phys.*, **2014**, 16, 7377-7384

9:40am **QC+AS+BI+MN-ThM6 On the Role of Acoustic Streaming in Particle Detachment Events at a QCM Surface**, ***Rebekka König***, *A. Langhoff, D. Johannsmann*, Clausthal University of Technology, Germany

A steady flow of liquid was observed above the surface of a quartz crystal microbalance (QCM) under conditions, where the oscillation amplitude exceeded 10 nanometers . The streaming flow occurs parallel to the displacement vector and is directed towards the center of the plate. It is expected to have applications in acoustic sensing, in microfluidics, and in micromechanics in a wider sense. The flow is caused by the nonlinear term in the Navier- Stokes equation, which can produce a nonzero time-averaged force from a periodic velocity field. Central to the explanation are the flexural admixtures to the resonator's mode of vibration. Unlike pressure-driven flows, the acoustically driven steady flow attains its maximum velocity at a distance of a few hundred nanometers from the surface. It is therefore efficient in breaking bonds between adsorbed particles and the resonator surface. As a side aspect, the flow pattern amounts to a diagnostic tool, which gives access to the pattern of vibration. In particular, it leads to an estimate of the magnitude of the flexural admixtures to the thickness-shear vibration.

[1] R. König, A. Langhoff, D. Johannsmann, *Physical Review E***2014**.

11:00am **QC+AS+BI+MN-ThM10 QCM for Particle Sizing and Beyond**, ***Adam Olsson***, *I.R. Quevedo, D. He, M. Basnet, W. Lee, N. Tufenkji*, McGill University, Canada **INVITED**

The dissipative energy loss of a quartz crystal microbalance (QCM) sensor is typically ascribed to the viscoelastic nature of the adsorbed material. While such an interpretation is suitable for thin homogeneous films, it is not *a priori* valid for discrete objects. As demonstrated recently, dissipation due to nanoparticle deposition can be described by the relative movement of the particles attached to the oscillating sensor surface. This particular dissipation behavior of nanoparticles gives rise to new experimental approaches to study colloidal transport, particle-surface interactions and particle properties.

In this presentation, we focus on QCM-D as a method to determine the size of deposited nanoparticles. The approach involves analysis of the change in dissipation per attached mass (i.e., the "*ΔD/Δf*-ratio") to predict a hypothetical full particle surface coverage that can be used to calculate an effective layer thickness of the particulate film; and this quantity, in turn, can be related to the average particle diameter. To validate the approach, we determined particle sizes using various types of nanoparticles with diameters ranging from ~ 5 nm to ~ 110 nm and compared the results with sizes obtained from dynamic light scattering (DLS) and transmission electron microscopy (TEM). We found that accurate particle sizing is possible, but requires firm coupling between the particle and the sensor surface. Hence, if the particle size is known, the approach can also be used to investigate the strength of the nanoparticle-surface interaction.

We will also describe our ongoing work where we are studying the QCM-D response to the deposition of anisotropic bacteriophage to determine their orientation on the surface. Bacteriophages are viruses that bind to and infect bacteria with high specificity and, thus, can be exploited in antimicrobial and biosensor applications. One challenge in functionalizing surfaces with bacteriophages is to control their orientation such that their binding sites remain exposed to the ambient medium. By studying how dissipation changes with phage surface coverage, it is possible to identify at which surface coverage phage-phage interaction occurs. This event compromises the phages ability to bind to bacteria, as evidenced by subsequent bacterial "capture" experiments and imaging, and thus is crucial for the performance of QCM-D based biosensors that utilize bacteriophage as a biorecognition element.

11:40am **QC+AS+BI+MN-ThM12 Full Experimental Proof of the Relationship between the Intrinsic Viscosity of DNA and the Acoustic Ratio of SAW and TSM Sensors**, ***Achilleas Tsortos***, IMBB-FORTH, Greece*, G. Papadakis,* NCSR-Demokritos, Greece*, E. Gizeli*, IMBB-FORTH & Univ. of Crete, Greece

Acoustic wave sensors are extensively used in biotechnology and biophysics in order, for example, to detect molecules in a solution, study an antibody-antigen interaction or the hybridization of DNA. Today, data analysis includes (a) the use of the Sauerbrey equation, in order to calculate the mass of the molecules attached on the surface of the acoustic device by use of frequency data and (b) the use of complicated mathematical models of the assumed 'film' formed by the attached molecules. In the second case information such as the rigidity modulus and viscosity of the 'film' can be calculated and comments can be made on the softness (viscoelasticity) of the added layer.

Here, we present an entirely different approach. Based on a theory developed earlier[1,2] we correlate the acoustic ratio R, to the intrinsic viscosity $[\eta]$ of the attached molecule. The acoustic ratio is the ratio of the amount of energy loss per attached unit mass – this is given as (ΔD/ΔF) in the TSM acoustic mode notification, or as (ΔA/ΔPh) in the SH-SAW mode and is readily obtained in each experiment. The *intrinsic* viscosity on the other hand, is a hydrodynamic quantity directly related to the size and shape of a biomolecule and can be determined independently through viscometry. In this study we present collected experimental data from a variety of case studies proving for the first time the semi-empirically assumed relationship $R\sim[\eta]$ in a general form. Data are presented for various shapes and sizes of DNA and other systems of biological interest. The case is made for two acoustic modes (thickness shear and surface horizontal) and for various frequencies in the range of 5-155 MHz.

Our analysis presents a paradigm shift and challenge; we claim that (label-free) structure probing is a much more improved method offering higher flexibility in design and interpretation of experimental assays. Detecting and monitoring in real time processes that involve structural changes but not necessarily mass changes and/or 'film' formation is a novel concept that can be readily applied in anything from DNA, RNA hybridization and detection of mutations to molecular machines (e.g. DNA Holliday junction) and protein/DNA/RNA interactions in the broad areas of biophysics, s tructural DNA nanotechnology and diagnostics.

Acknowledgement: the REGPOT-InnovCrete/EU-FP7 (Contract No. 316223) for financial support.

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1. A. Tsortos, et al., *Biophys. J.* 2008, 94:2706

2. A. Tsortos, et al., *Biosens. Bioelectron.* 2008, 24:836

12:00pm **QC+AS+BI+MN-ThM13 Characterization of the Conformation of Linker-Suspended Proteins at Surfaces through Acoustic Ratio Measurements**, ***Electra Gizeli***, IMBB-FORTH & Univ. of Crete, Greece, *D. Milioni,* IMBB-FORTH, Greece, *G. Papadakis,* NCSR-Demokritos, Greece, *A. Tsortos*, IMBB-FORTH, Greece

Characterization of protein shape and orientation following surface binding is an area of great interest in biophysics with many applications in chemistry and nano/biotechnology. Techniques such as ellipsometry and AFM have been extensively used for providing such information. A lot of effort has also been put with acoustic sensors; results in this case though depend greatly on the data interpretation model employed. An important question is always the preservation of protein integrity/form.

In this work we employ acoustic devices based on a QCM geometry at 35 MHz. The acoustic ratio ΔD/ΔF, i.e., the dissipation over frequency change of the shear wave has been employed in our analysis. We have previously shown[1] that as a tool, this ratio provides valuable information regarding the conformation of surface attached DNA molecules; we have also employed this approach in the design of DNA assays for diagnostic purposes, including detection of sequence targets in real samples[2].

Here we expand this methodology in proteins; streptavidin is used as a case study for characterizing spherical protein immobilization on an acoustic device. Good control of the binding mode was achieved by changing the distance of the protein from the surface, ranging from zero (direct physisorption) to several nm, using anchor molecules. In this way we can manipulate the degree of surface interference to the protein structure. Our results clearly show that direct protein adsorption is a multistep process resulting in very low acoustic ratio, in agreement with the literature. However, we show for the first time that suspending the protein away from the surface from a single point through a variable-length linker, gives an entirely different picture; the process is a single-step event, as judged from D-F plots, and the resulting acoustic ratio is much higher (order of magnitude) than that obtained in physisorption. The effect of the linker length on the apparent acoustic ratio is analyzed. This approach gives more reliable and different information regarding the protein shape than do simple physisorption protocols and interpretation models involving notions such as 'film' formation etc.

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1. A. Tsortos, et al., *Biosens. Bioelectron.* 2008, 24:836; A. Tsortos et al., *Biophys. J.* 2008, 94:2706

G. Papadakis et al., *Anal. Chem.* 2012, 84:1854; G. Papadakis et al., *Scientific Rep.* 2013, 3:2033

Surface Modification of Materials by Plasmas for Medical Purposes Focus Topic
Room: 315 - Session SM+AS+BI+PS-ThM

Plasma Processing of Antimicrobial Materials and Devices
Moderator: Heather Canavan, University of New Mexico, Morgan Hawker, Colorado State University

8:00am **SM+AS+BI+PS-ThM1 Plasma Polymers: Dogma, Characteristaion and Challenges**, ***Sally McArthur***, Swinburne University of Technology, Australia **INVITED**

Plasma polymers, the dogma tells us are densly cross-linked, pinhole free films that adhere to virtually any dry surface. But when you are working at low power and trying to retain specific functional groups within your films, is this still true? How does environment (pH, salt concentration) effect film behaviour and what do respnses to change in environment tell us about the nature of these films? This talk will explore methods for studying the physicochemical behaviours of plasma polymer films and discuss how these films can be manipulated address specific biomaterials challenges.

8:40am **SM+AS+BI+PS-ThM3 The Role of Plasma Surface Modification in Antimicrobial Thin Films and Strategies**, ***Renate Foerch***, FhG-ICT-IMM, Germany **INVITED**

"Delivery on demand" has become a key issue in the development of solutions for bacterial infection and the evolution of resistance. Antimicrobial bioactive coatings may be thin layers, scaffolds or hybrid materials with chemically immobilized or physically embedded antimicrobial substances that act while tethered to a surface or that are released either passively or upon a stimulus. Examples include burst release systems of an antimicrobial from plasma polymerised thin films that have fed into a recent efforts aiming to develop, characterize and evaluate nanocomposite coatings consisting of thin films, nanoparticles and nanocarrier systems. The nanocomposite coatings are formulated to respond to specific changes in the surrounding environment. The work to be described is part of a European-Australian effort to investigate new strategies to combat microbial infection; it draws expertise from plasma assisted technologies and wet chemical post plasma attachment of responsive nanocontainers carrying an antimicrobial to treat bacterial infection.

9:20am **SM+AS+BI+PS-ThM5 Plasma Modification of Drug-Eluting Materials for Localized Action at Medical Device Interfaces**, *J. Joslin, A. Pegalajar-Jurado, M.J. Hawker, E.R. Fisher,* ***Melissa Reynolds***, Colorado State University **INVITED**

To direct protein and cellular behavior at the surface of synthetic materials, both localized chemical signaling and control over surface properties are required. To achieve requisite drug delivery dosages, hydrophobic polymers are often employed that slowly elute a therapeutic agent from the bulk material into systemic circulation. However, the surface free energy of the hydrophobic material can lead to deposition of undesired proteins and activation of the clotting. To overcome these challenges, advanced material platforms are needed to achieve localized therapeutic action and customizable surface properties. Herein, we present the development of $H_2O(v)$ plasma-treated PLGA-nitric oxide (NO) releasing materials. NO is a well-established anti-platelet and anti-microbial agent, and the NO release rate can be controlled by the hydrophobic nature of the bulk material where it was incorporated. Plasma treatment conditions were optimized to maintaining the NO release function while rendering the surface hydrophilicity. Despite the plasma conditions employed, the material retained 80-90% of the *S*-nitrosothiol content, while the NO release profiles were unaltered compared to the control. The change in the surface wettability was confirmed by water contact angle measurements. Extensive surface (XPS) and bulk (ATR FT-IR) chemical characterization demonstrated that the changes in wettability was due to the implantation of O-containing surface functional groups such as carbonyl and hydroxyl groups. In addition, optical profilometry analysis confirmed no statistically significant changes in the surface roughness compared to the control. Furthermore, the materials show minimal hydrophobic recovery after several days stored at -20°C. By combining both chemical signaling and surface treatments into one material, we expect to reduce activation of clotting cascade and enhance the biocompatibility of the materials.

11:00am **SM+AS+BI+PS-ThM10 Plasma Treated Substrates Reduce Protein Adsorption**, ***Marvin Mecwan***, *J. Stein, W. Ciridon,* University of Washington, *X. Dong,* Eli Lilly and Company, *B. Ratner*, University of Washington

Proteins irreversibly adsorb onto surface, causing losses from solution, denaturation, as well as aggregation. Hence, there have been recent efforts in the pharmaceutical industry to addressing the manufacture, packaging and delivery of protein-based pharmaceuticals. We propose the use of radio-frequency (RF) plasma deposition to create coatings on substrates relevant to the pharmaceutical industry—glass, stainless steel and cyclic olefin polymer (COP). The monomers of choice were acrylic acid (AA) and tetraglyme (TG) (hydrophilic), and perfluoropropylene (C3F6) and perfluoromethyl vinyl ether (C3F6O) (hydrophobic). All monomers were successfully plasma coated on all substrates, and did not delaminate as was determined from survey and detailed ESCA scans. Furthermore, no peaks associated with the substrates were seen in the scans, which indicate that the plasma coating are at least 100Å thick. Protein adsorption studies were carried out using 0.1mg/mL solution of I-125 tagged bovine IgG by adsorbing the tagged protein on the plasma treated substrates for an hour. All hydrophilic monomer plasma treated substrates had lesser protein adsorbed on their surfaces (< 2ng/cm^2) as compared to hydrophobic plasma treated substrates (10-14 ng/cm^2). This is in comparison to untreated controls that had 200-300 ng/cm^2 protein adsorbed on the surface. Furthermore, following ISO 10993-5 guidelines, by performing cytotoxic studies using NIH-3T3 fibroblasts all plasma treated substrates were determined to be non-cytotoxic. Hence, these results indicate that radio-frequency plasma treatment could lead to a new generation of surfaces that will be particularly effective for protein manufacture, storage and delivery. Future studies will be aimed at determining plasma coating thickness, protein aggregation assessment as well as studying the bonding strength of the proteins to the plasma treated surfaces.

11:20am **SM+AS+BI+PS-ThM11 Modification of Porous Materials by Low Temperature Plasma Treatment to Achieve Low-Fouling Membranes**, ***Adoracion Pegalajar-Jurado***, *B.D. Tompkins, E.R. Fisher*, Colorado State University

Artificial porous polymeric membranes are used in many applications including water filtration systems and devices to treat blood for a broad variety of therapeutic purposes. In water filtration systems, membranes are used to remove colloidal particles and organic molecules from the watercourse and, in medical treatments, they function primarily to eliminate toxins from the blood before it is returned to the patient's body. Although these are very different applications, both are affected by membrane fouling from proteins, toxins, bacteria, and cells, which significantly decrease flow through the porous material. Surface modification techniques that retain the desired bulk properties are the ideal method for obtaining low-fouling membranes, thus extending their life-time in applications where they are exposed to fouling conditions. Here, we will present the properties of polysulfone ultrafiltration membranes subjected to H_2O plasma and their performance when exposed to proteins and bacteria. Plasma treated membranes showed enhanced hydrodynamic characteristics (i.e. increase in water flux) as a result of their high hydrophilicity. Notably, hydrophilic characteristics were retained for more than six months, ensuring top-shelf stability of the surface treatment. In terms of protein fouling performance, treated membranes show less bovine serum albumin adsorption than untreated membranes and cleaning of treated fouled membranes yields 70-90% flux recovery depending on plasma treatment time. This surface modification provides a mechanism for extending the life-time of the membranes.

11:40am **SM+AS+BI+PS-ThM12 Immobilized Laminin Concentration Gradients on Electrospun Fiber Scaffolds for Controlled Neurite Outgrowth**, ***Nicole Zander***, US Army Research Laboratory, *T. Beebe Jr.*, University of Delaware

Neuronal process growth is guided by extrinsic environmental cues such as extracellular matrix proteins (ECM). Recent reports have described that the growth cone extension is superior across gradients of the ECM protein laminin compared to growth across uniformly distributed laminin. In this work, we have prepared gradients of laminin on aligned electrospun nanofibers for use as substrates for neuronal growth. The substrates therefore presented both topographical and chemical guidance cues. Step gradients were prepared by the controlled robotic immersion of plasma-treated polycaprolactone fibers reacted with N-hydroxysuccinimide into the protein solution. The gradients were analyzed using x-ray photoelectron spectroscopy and confocal laser scanning microscopy. Gradients with a dynamic range of protein concentrations were successfully generated and neurite outgrowth was evaluated using neuron-like PC12 cells. After 10 days of culture, PC12 neurite lengths varied from 32.7 ± 14.2 µm to 76.3 ± 9.1 µm across the protein concentration gradient. Neurite lengths at the highest concentration end of the gradient were significantly longer than neurite lengths observed for cells cultured on samples with uniform protein coverage. Gradients were prepared both in the fiber direction and transverse to the fiber direction. Neurites preferentially aligned with the fiber direction in both cases indicating that fiber alignment has a more dominant role in controlling neurite orientation, compared to the chemical gradient.

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.

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

266401 (2012).

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).

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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**,

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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.

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Helium Ion Microscopy Focus Topic
Room: 316 - Session HI+2D+AS+MC-ThA

Nanoengineering with Helium Ion Beams
Moderator: Armin Gölzhäuser, University of Bielefeld, Germany, David C. Joy, University of Tennessee, Oak Ridge National Laboratory

2:20pm **HI+2D+AS+MC-ThA1 Helium Ion Microscopy (HIM) Technology for Imaging, Characterization, and nano-Fabrication for nano-Device Materials and Structures**, ***Shinichi Ogawa***, NeRI, AIST, Japan **INVITED**

Several unique applications of a helium ion microscopy (HIM) technology have been studied. In comparison with electron, helium ion has larger cross section, and it realized HIM observation with less current because of higher efficiency of secondary electron generation with maximum distribution energy of 1 eV [1], a few eV in a SEM case, for imaging, which results in less power implant (less thermal damage input) into samples. Utilizing these features, a low dielectric constant material pattern of 70 nm line with less deformation (thermal damage) and a Cu metal line underneath a 130 nm dielectric of band gap of a few eV were imaged [2]. Luminescence from a SiO_2 sample was detected at imaging conditions [3], in which no damage was observed by a transmission electron microscopy (TEM) - electron energy loss spectroscopy method [4]. As one of nano-fabrication applications, we found that a helium ion irradiation using the HIM functionalizes a gate control of carrier conduction in a single-layer graphene at an appropriate amount of helium ion dose to graphene which enable gate bias control of current with an on-off ratio of two orders of magnitude at room temperature [5], [6]. A few nm diameter tungsten particles were deposited onto a TEM sample under the helium ion beam irradiation in $W(CO)_6$ gas atmosphere with high special resolution accuracy, which realized precise electron tomography and re-construction [7], and tungsten pillars of a few um height with 40 nm diameter were formed with a straight hole of a few nm diameter through a center of the pillars [8]. The research on graphene material is granted by JSPS through FIRST Program initiated by CSTP.

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3:00pm **HI+2D+AS+MC-ThA3 MEMS Temperature Controlled Sample Stage for the Helium Ion Microscope**, ***Jose Portoles***, *P.J. Cumpson*, Newcastle University, UK

The Helium microscope allows the imaging of samples with magnifications beyond those of electron microscopes with the added advantages of directly imaging insulators without being so critically dependent on a need to conductive coating the samples. This facilitates the imaging of for instance organic structures without the need of surface modification. The large depth of focus allows simultaneously focusing details of the sample at different depths. When using a temperature controlled stage this allows the samples to stay focused as thermal expansion produces vertical displacements of the sample surface, however due to the large magnifications in-plane thermal expansions are still an issue. We have investigated a solution based on a thermally actuated X-Y MEMS stage by exploiting the ability of MEMS actuators to provide smooth electronic control of lateral displacements in the micron range in order to compensate for lateral thermal expansion at the point of observation. The difficulties involved in producing relatively large out of plane displacements with a MEMS device can be neglected due to the large instrumental depth of focus. The device we present has been fabricated using a “silicon on insulator” (SOI) MEMS process, and can be driven at low voltages and currents using a standard vacuum feedthrough to the instrument's analysis chamber and compensate lateral thermal expansion in order to keep any spot on a small specimen in the field of view at high magnifications. The small size of the heating stage makes it rapid in its thermal response.

3:20pm **HI+2D+AS+MC-ThA4 Monte Carlo Simulations of Focused Neon Ion Beam Induced Sputtering of Copper**, ***Rajendra Timilsina***, *P.D. Rack,* The University of Tennessee Knoxville*, S. Tan, R.H. Livengood*, Intel Corporation

A Monte Carlo simulation has been developed to model the physical sputtering and nanoscale morphology evolution to emulate nanomachining with the Gas Field Ion Microscope. In this presentation, we will present experimental and simulation results of copper vias milled by a focused neon ion beam. Neon beams with a beam energy of 20 keV and a Gaussian beam profile with full-width-at-half-maximum of 1 nm were simulated to elucidate the nanostructure evolution during the physical sputtering of high aspect ratio features. In this presentation we will overview our simulation attributes which includes an evolving real-time sputtered via profile considering both thesputtered and re-deposited material. The sputter yield and sputter profile vary with the ion species and beam parameters and are related to the distribution of the nuclear energy loss in the material. We will also illustrate how the effective sputter yield is aspect-ratio dependent due to the change in the effective escape angle of the sputtered species. Quantitative information such as the sputtering yields, dose dependent aspect ratios and resolution-limiting effects will be discussed. Furthermore, we will show that the calculated nuclear energy loss and implant concentration ahead of the sputtering front correlates to observed damage revealed by transmission electron microscopy.

4:00pm **HI+2D+AS+MC-ThA6 Circuit Edit Nanomachining Study using Ne+ & He+ Focused Ion Beam**, ***Richard Livengood***, *S. Tan*, Intel Corporation **INVITED**

FIB nanomachining has been used extensively for over 20 years for the purpose of rewiring integrated circuits to validate design changes, isolate process faults, and generate engineering samples. During this time frame, the minimum feature size of an IC (Moore's Law) has scaled from 500nm to 14nm (36X) compared with ~6X scaling of Ga+ FIB. As a result FIB nanomachining capabilities have been steadily erroding over the last several generations, limiting the types of circuit modifications that can be sucessfully completed. There are however, several promising new ion beam scaling R&D initiatives that provide hope of enabing further nanomachining scaling into the sub 10nm process node.

One such technology is GFIS (gas field ion source) technology. He+ GFIS based FIBs have been successfully used to image with sub 0.5nm resolution and nanomachine sub 10 nm structure in Au, Graphine, and other thin film structures.[1, 2, 3] More recently He+ and Ne+ GFIS sputtering properties have been studied for nanomachining in bulk semiconductor films.[4] In this paper, we will show our latest results on GFIS FIB GAE (gas assisted etch) nanomachining and IBID properties and electrical invasiveness impact.

References

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4:40pm **HI+2D+AS+MC-ThA8 Evaluation of EUV Resist Performance below 20-nm CD using Helium Ion Lithography**, *D.J. Maas,* TNO Technical Sciences, Netherlands, ***Nima Kalhor***, TU Delft, Netherlands, *W. Mulckhuyse, E. van Veldhoven,* TNO Technical Sciences, Netherlands, *A. van Langen–Suurling, P.F.A. Alkemade,* TU Delft, Netherlands, *S. Wuister, R. Hoefnagels, C. Verspaget, J. Meessen, T. Fliervoet*, ASML, Netherlands

For the introduction of EUV lithography, development of high performance EUV resists is of key importance. This development involves studies into sensitivity, resolving power and pattern uniformity. We have used a sub-nanometer-sized 30 keV helium ion beam to expose chemically amplified (CAR) EUV resists.

There are remarkable similarities in the response of resists to He$^+$ ions and EUV photons. Both primary particle beams traverse the resist and meanwhile interact with the target atoms. The low backscattering of the He$^+$ ions results in ultra-low proximity effects, which is similar to EUV exposure s . Absorption of an EUV photon creates a high-energy electron that relaxes by the excitation of Secondary Electrons (SEs). A collision of a 20-30 keV helium ion with a target atom directly releases low-energy SEs. Each ion scatters several times in the resist layer, thus enabling resist exposures at very low doses per CH . The energy spectra of SEs generated by EUV and He$^+$ are remarkably alike. These SEs, in turn, activate the resist.

In this paper we show 30 keV He$^+$ ions exposures of contact holes and lines with a CD of 8 – 30 nm at 20 nm half-pitch in a chemically amplified EUV resist. We will demonstrate the potential of using He$^+$ ion lithography [1,2] in the study of EUV resists.

[1] V. Sidorkin et al., *Sub-10-nm nanolithography with a scanning helium beam*, J. Vac. Sci. Technol. B **27**, L18 (2009)

[2] D. Maas et al., *Evaluation of EUV resist performance below 20nm CD using helium ion lithography,* SPIE Proc. **9048**, 90482Z (2014)

5:00pm **HI+2D+AS+MC-ThA9 Helium Ion Beam Lithography for Nanoscale Patterning**, *X. Shi,* University of Southampton, UK, *D.M. Bagnall,* University of New South Wales, UK, ***Stuart Boden***, University of Southampton, UK

Electron beam lithography (EBL), the modification of thin films of resist by a focused beam of electrons to create a pattern that is subsequently transferred into the substrate, is a key technology in the development of nanoscale electronic devices. However, with the demand for ever smaller features and pattern dimensions, new lithographic techniques are required to extend beyond existing limits of EBL. One such emerging technology is helium ion beam lithography (HIBL), driven by the development of the helium ion microscope, a tool capable of producing a high intensity beam of helium ions focused to a sub-nanometer spot [1]. Preliminary studies on HIBL using typical EBL resist materials such as PMMA and HSQ have shown that HIBL has several advantages over EBL, including a smaller spot size (potentially leading to higher resolution patterning) and a decrease in the exposure dose required and so the potential for faster pattern definition and therefore higher throughput. Furthermore, proximity effects, which are caused by beam scattering leading to inadvertent exposure of surrounding material, and are problematic when producing high density patterns in EBL, are massively reduced in HIBL [2], [3].

Here, the latest results from an experimental investigation into the HIBL technique will be presented. Areas of PMMA films of various thicknesses are exposed to different helium ion doses. After subsequent development in MIBK/IPA, atomic force microscopy is used to measure residual layer thickness in order to generate exposure response curves for different initial thicknesses of resist. High sensitivity is confirmed with full exposure of 50 nm thick layers achieved with a helium ion dose of only ~2 μC/cm^2. Experiments to characterise minimum feature size and proximity effects are currently underway. The use of other high resolution resists will also be investigated with the aim of providing a thorough assessment of the capabilities and limitations of this emerging nano-patterning technique.

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5:20pm **HI+2D+AS+MC-ThA10 Sub-100nm Nanofabrication using Helium and Neon Ion Beams**, ***James Sagar***, *C. Nash, N. Braz, T. Wootton, M.J.L. Sourribes, T.-T. Nguyen, R.B. Jackman, P.A. Warburton*, London Centre for Nanotechnology, UK

Sub-100nm Nanofabrication using Helium and Neon Ion Beams

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Using a Zeiss Orion NanoFab we have created sub-100nm devices for experiments in quantum electronics and nanophotonics. The Orion NanoFab has the ability form an ion beam with either helium or neon gas. This makes the Nanofab a much more versatile instrument for nanofabrication since large area mills can be performed using Ne without the need for a Ga FIB column. The use of a Ne gas field ion source (GFIS) in the Orion NanoFab allows fabrication of sub-100nm devices on timescales comparable to that of conventional liquid Ga FIB but with considerably enhanced fidelity due to an increased sputter yield (ten times greater than that of He) whilst retaining a small probe size (≤ 5nm). Using a Ne ion beam we have fabricated two kinds of nanoscale superconducting devices: a superconducting nanowire based on a compound low-T_C superconductor; and an array of nanoscale Josephson junctions based on a compound oxide high-T_C superconductor. The use of an inert-gas ion species in these devices is extremely important as Ga implantation into superconducting materials has previously been shown to suppress superconductivity. The extremely small probe size of the He GFIS has allowed us to create sub-20nm apertures in a variety of materials. Sub-20nm apertures in InAs nanowires and in graphene have been fabricated for experiments in quantum coherent electronics and quantum nanophotonics respectively.

Fundamentals & Biological, Energy and Environmental Applications of Quartz Crystal Microbalance Focus Topic
Room: 317 - Session QC+AS+BI+MN-ThA

Applications of QCM
Moderator: Electra Gizeli, IMBB-FORTH, Heraklion, Crete,Greece, Adam Olsson, McGill University, Canada

2:20pm **QC+AS+BI+MN-ThA1 Permeability of a Model Stratum Corneum Lipid Membrane**, ***Daeyeon Lee***, University of Pennsylvania **INVITED**

The stratum corneum (SC), composed of corneocytes and intercellular lipid membranes, is the outermost layer of the epidermis, and its main function is the regulation of water loss from the skin. The major components of the SC lipid membranes are ceramides (CER), cholesterol (CHOL), and free fatty acids (FFA), which are organized in multilamellar structures between corneocytes. The intercellular SC lipid membrane is believed to provide the main pathway for the transport of water and other substances through the skin. While changes in the composition of the SC lipid membranes due to intrinsic and/or extrinsic factors have been shown to affect the organization of the lipid molecules, little is known about the effect of compositional changes on their water permeability. In this talk, I will present our results on the effect of composition on the permeability of a model SC lipid membrane consisting of ceramide, palmitic acid, and cholesterol using a quartz crystal microbalance with dissipation monitoring (QCM-D). The QCM-D method enables the direct determination of the diffusivity (D), solubility (S), and permeability (P) of water through the model SC lipid membranes. In the first part, I will discuss the effect of membrane composition on the water permeability of the model SC lipid membrane. We find that D and S weakly depend on the chain length of saturated fatty acids, while P shows no significant dependence. In contrast, the saturation level of free fatty acids and the structure of ceramide have significant influence on D and S, respectively, resulting in significant changes in P. In the second part of the talk, I will present our recent work on the effect of common anionic surfactants on the water permeability of the model SC lipid membrane. Particularly, the effect of sodium dodecyl sulfate (SDS) and sodium lauryl ether sulfate (SLES) with one or three ethoxy groups on the water permeability of the model SC lipid membrane is compared.

3:00pm **QC+AS+BI+MN-ThA3 Investigation of Interaction between a Monoclonal Antibody and Solid Surfaces via Multiple Surface Analytical Techniques**, ***Xia Dong***, *C.A.J. Kemp, Z. Xiao*, Eli Lilly and Company

The interaction between proteins and surfaces is an important topic in the field of biomaterials. With the development of monoclonal antibody products, there is increasing interest in understanding the nature of the interactions between antibodies and the solid surfaces they contact during manufacturing processes and storage. In this study, a monoclonal antibody was introduced to quartz crystal microbalance (QCM) substrates coated with gold, stainless steel and silicon carbide. The samples were characterized by multiple surface analytical techniques, including TOF-SIMS and XPS. The preliminary XPS results suggest that the protein adsorbed at higher concentration on gold than on stainless steel and silicon carbide, while nitrogen concentration detected on stainless steel is slightly higher than on silicon carbide. This is generally consistent with the QCM results. TOF-SIMS spectra also suggest that the interaction between the antibody and three substrates is not the same. The fragmentation patterns detected in the TOF-SIMS spectra obtained from silicon carbide and stainless steel are similar to each other, but they are different from those detected on gold. The interaction between the antibody and stainless steel coupons will be further studied to understand the influence of surface morphology.

3:20pm **QC+AS+BI+MN-ThA4 Combining Spectroscopic Ellipsometry and Quartz Crystal Microbalance to Study Biological Hydrogels – Towards Understanding Nucleo-Cytoplasmic Transport**, *N.B. Eisele, S. Ehret, R. Zahn,* CIC biomaGUNE, Spain, *S. Frey, D. Gorlich,* MPI Biophysical Chemistry, Germany, ***Ralf Richter***, CIC biomaGUNE & Université Grenoble Alpes & MPI Intelligent Systems, Spain

Nature has evolved hydrogel-like materials that are exquisitely designed to perform specific biological functions. An example of such a material is the nuclear pore permeability barrier, a nano-sized meshwork of intrinsically disordered proteins (so called FG nups) that fills the nuclear pores (i.e. the roughly 40 nm wide channels across the nuclear envelope) and controls the entry of macromolecules into the nucleus of eukaryotic cells. The permeability barrier exhibits a unique selectivity in transport: very small molecules can cross the barrier efficiently, while larger objects are delayed or blocked unless they are bound to specialized proteins, so called nuclear transport receptors (NTRs). How size and species selectivity are encoded in the hydrogel-like properties of the permeability barrier is currently not well understood.

We have developed monolayers of end-grafted FG nups as a nano-scale model system of the permeability barrier. The planar geometry of this well-defined biomimetic film affords detailed and quantitative characterization – not accessible for the native system - with a toolbox of surface-sensitive characterization techniques. In particular, we present the application of the *in situ* combination of quartz crystal microbalance (QCM-D) and spectroscopic ellipsometry (SE) to quantify film thickness, hydration and viscoelastic properties as a function of protein surface density.

We will present how this experimental data, combined with polymer theory, allows us to better understand the relationship between the supramolecular organization and dynamics of the permeability barrier, its physico-chemical properties and its biological function. We demonstrate that attractive interactions between FG nups play an important role in tuning the assembly and morphology of FG nup meshworks, and highlight that even rather weak interactions – typically a few *kT* per biopolymer chain – have functional importance. We show also how the interaction between NTRs and FG nup meshworks is tuned to afford strong enrichment and at the same time rapid entry and exit of NTRs in the permeability barrier, thereby facilitating NTR translocation.

Taken together, these studies contribute important information to understand the mechanism of size-and species-selective transport across the nuclear pore permeability barrier. The mechanistic insight gained should be useful towards the design of bioinspired species-selective filtering devices. Moreover, the presented procedures for the acquisition and analysis of combined QCM-D/SE data are broadly applicable for the characterization of ultrathin biomolecular and other polymer films.

4:00pm **QC+AS+BI+MN-ThA6 Probing Nanoparticle-Biofilm Interactions using Quartz Crystal Microgravimetry and Complementary Surface-sensitive Methods**, ***Kaoru Ikuma****, University of Massachusetts, *Z. Shi, A.V. Walker,* University of Texas at Dallas, *B.L.T. Lau*, University of Massachusetts

The environmental fate and transport of nanoparticles (NPs) have been a rising topic of concern due to the increased use of nanotechnology. Recent studies have shown that NPs are likely to interact readily with and accumulate in environmental biofilms. Biofilms are a ubiquitous form of microbial presence where cells attached on solid surfaces are surrounded by a sticky matrix of extracellular polymeric substances (EPS). The EPS matrix is considered to be highly heterogeneous and chemically complex. Polysaccharides and proteins are known to be major constituents of EPS and may greatly impact the likelihood of interactions occurring between NPs and biofilms.

In this study, we examined the deposition of NPs onto surface-immobilized proteins to determine the importance of protein-rich domains in the interfacial interactions between NPs and biofilms. Such interfacial processes are the initial and potentially rate-limiting step in NP-biofilm interactions. The deposition kinetics and extent of model hematite (α-Fe$_2$O$_3$) NPs onto protein-coated silica surfaces were quantitatively measured by quartz crystal microbalance with dissipation (QCM-D). Model proteins including bovine serum albumin (BSA) and lysozyme as well as bacterial total proteins were used herein. The proteins were initially adsorbed onto either negatively-charged bare or positively-charged poly-L-lysine (PLL)-precoated silica sensors to assess the effects of the orientation of surface-immobilized proteins. In addition to QCM-D, other complementary surface-sensitive techniques such as Kelvin probe force microscopy and time-of-flight secondary ion mass spectrometry (TOF SIMS) were used to characterize the mechanisms of interaction between the NPs and the protein-coated surfaces.

QCM-D results indicated that for all tested proteins, the total deposition extent of hematite NPs was significantly greater on protein layers that were adsorbed onto bare silica compared to PLL-precoated silica sensors. TOF SIMS results showed that the amino acid profiles of the topmost surface of the protein layers on bare and PLL-precoated silica sensors were distinctly different, suggesting that NP deposition was greatly influenced by the orientation of the surface-immobilized proteins. Both the extents and rates of NP deposition were also dependent on the type of model protein. Based on the surface charge, topography, and hydrophobicity characterization results, the observed interfacial interactions between hematite NPs and surface-immobilized proteins appeared not to be controlled by one dominant interaction force but by a combination of electrostatic, steric, hydrophobic, and other interactions.

4:20pm **QC+AS+BI+MN-ThA7 Association and Entrapment of Membrane-Targeted Nanoparticles with Different Binding Avidity: A QCM-D and sIngle Particle Tracking Study**, ***Anders Lundgren‡***, *B. Agnarsson, S. Block, F. Höök*, Chalmers University of Technology, Sweden

Nanoparticles specifically targeted to receptors in the cell membrane are interesting for various applications such as intracellular delivery and visualization of diffusing membrane proteins, so-called single particle tracking. These diverse applications require particles optimized to display different binding properties: In this model study we investigated the effect of particle size and ligand density on the association rate and mobility/entrapment of biotin functionalized core-shell nanoparticles to supported lipid bilayers sparsely modified with streptavidin. Gold-PEG core-shell nanoparticles were synthesized with two different core sizes, 20 and 50 nm in diameter, and a shell (10 nm) of mixed uncharged, negatively charged and biotinylated PEG-ligands, the biotin content varied from one to several hundreds per particle. Particle binding was examined on the ensemble level using QCM-D and on single particle level using novel light scattering microscopy that will be detailed. At physiological salt conditions, binding of 50 nm particles were weakly dependent on the number of

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*** QCM Focus Topic Young Investigator Award**

displayed biotin ligands, whereas the association of 20 nm particles were strongly attenuated in direct relation to the ligand density. At low salt conditions, binding of the larger particles resembled that of the smaller particles, with a strong dependence on ligand density. PEGylated particles without biotin-ligands did not bind at any condition. Thus, it was concluded that specific particle affinity is strongly attenuated by particle size and surface charge due to different interaction potential between the particle and the surface. On the contrary, no dependence on particle size was observed for the mobility of single particles displaying diffusion constants close to 0.4 or 0.8 μm^2/s irrespective of particle size, which was similar to ensemble measurements using FRAP data on FITC-labelled streptavidin (0.5 μm^2/s). Only particles with a single surface tether show continuous diffusion; after formation of a second surface bond particles got quickly entrapped and formed additional bonds. In QCM-D measurements, this was manifested by a continuously decreasing dissipative response per particle for binding of particles with increasing ligand density. Together, QCM-D and particle tracking data indicates that two different mechanisms may lead to particle trapping and ultimately particle wrapping: For very high ligand densities membrane receptors in the membrane diffuse to and partly wraps around immobile particles, whereas for intermediate ligand densities the diffusion and dynamics of the particles themself facilitate the formation of additional surface bonds and eventual wrapping.

4:40pm **QC+AS+BI+MN-ThA8 Complementary Chemiresistor and QCM Studies of Biomacromolecules as Sorptive Materials for Vapor Sensing**, ***Kan Fu****, X. Jiang, B.G. Willis*, University of Connecticut

Biomolecules are integral components of current sensing and diagnostic technologies including enzymatic glucose sensors, DNA microarrays, and antigen-antibody assays. The use of biomolecules in non-biological situations, however, is a burgeoning new field that may break the existing boundaries of biomolecule applications in exclusively biological context. Extensive studies have already been performed in bioelectronics using small biomolecules and biomacromolecules, revealing promising results regarding charge transport and conformation dependence. In the area of sorptive chemical sensors, biomacromolecules have inherent advantages over conventional synthetic polymers. DNA oligomers have precisely defined sequences through synthesis, they are monodisperse, and they can self-assemble into nanoscale structures. These features make them interesting for vapor sensing of small molecules.

In this work, a series of 8 custom-designed, single-strand DNA (ssDNA) were integrated with chemiresistors and QCM to make sensors. Chemiresistor sensors were made by depositing gold nanoparticles functionalized with ssDNA molecules onto microfabricated electrodes, and QCM sensors were made by depositing films of ssDNA on quartz crystals. While chemiresistors give high signal-to-noise ratios and significantly better limits of detection (LODs) and may eventually be the transducer for practical applications, QCM is a purely mass-sensitive technique that reveals fundamental absorption properties in terms of partition coefficients. By exposing these sensors to a series of organic vapors, the resistance change and mass change of the two sensor platforms can be compared. It is demonstrated that, similar to previous comparative studies of gold nanoparticles functionalized with small organic thiols and synthetic polymer modified QCM crystals, the nanoparticle-based chemiresistor response follows the QCM-traced mass change. The studies show that sorption and conductance modulation mechanisms of vapors on biomolecules are similar to sensors with small organic molecules, but the polarity preference is very different. A model relating partition coefficients K in and chemiresistor responses $\Delta R/R$ is thereafter suggested to account for the links between these 2 sensing systems. It needs to be noted that points which deviate from the modeled trends are likely the result of more complex vapor-material interactions. From here, we demonstrate that DNA oligomers are rich in diversity, which may qualify these materials for array-based and specific sensing applications. It also establishes QCM as a useful complementary tool for evaluating materials for various sensing systems.

5:00pm **QC+AS+BI+MN-ThA9 The Evolution of Complex Artificial Cell Membranes: Combining Patterned Plasma Polymers and Supported Lipid Bilayers**, ***Hannah Askew****, S.L. McArthur*, Swinburne University of Technology, Australia

Supported lipid bilayers (SLBs) have provided researchers with stable and reproducible platforms to recreate cell membrane environments. Such models are useful for studying a variety of processes including cell signalling and drug-membrane interactions. Unfortunately, current models are lacking in their ability to mimic complex micro and nanoscale architectures found within native cell membranes. Many methods of SLB patterning have emerged to form these complex structures. In particular pre-patterned substrates combined with vesicle collapse are of great interest as they eliminate complications associated with preserving membrane integrity during patterning. Plasma polymerisation provides a versatile, one step, dry method of creating thin films of different chemistries on almost any substrate. Successful bilayer formation on such coatings would be beneficial for promoting specific organisation in complex SLB systems using patterned surface chemistries. In the initial stages of this work we studied the effect of plasma polymer chemistry on the lipid structures formed using vesicle collapse. DOPC lipid vesicles were introduced to commonly used coatings formed from plasma polymerised allylamine (ppAAm) and acrylic acid (ppAAc). The coatings were characterised using X-Ray Photoelectron Spectroscopy (XPS), contact angle and Quartz Crystal Microbalance with Dissipation (QCM-D) techniques. Lipid interaction kinetics and lipid mobility were characterised using QCM-D and Fluorescence Recovery after Photobleaching (FRAP) respectively. It was shown that a variety of lipid structures including mobile bilayer can be formed on ppAAc using pH alone to control electrostatic interactions. ppAAm formed immobile vesicular layers under all conditions tested and could therefore be used as a barrier to confine fluid areas of bilayer. Work is now being undertaken to create single and dual plasma polymer patterns on both glass and silicon wafer. Standard photolithography and ion beam methods will be employed to pattern on both a micro and nanoscale. In this way plasma polymer patterns may enable the formation of increasingly complex SLB architectures.

5:20pm **QC+AS+BI+MN-ThA10 Applications of QCM in Industrial R&D**, ***Andrey Soukhojak***, The Dow Chemical Company

An overview of diverse applications of QCM enabled by its unparalleled sensitivity to mass and viscoelastic properties of thin samples in R&D of The Dow Chemical Company will be presented.

Surface Modification of Materials by Plasmas for Medical Purposes Focus Topic
Room: 315 - Session SM+AS+BI+PS-ThA

Plasma Processing of Biomemetic Materials
Moderator: Sally McArthur, Swinburne University of Technology, Adoracion Pegalajar-Jurado, Colorado State University

2:20pm **SM+AS+BI+PS-ThA1 The Chemistry of Plasma Modified 3D Biomaterials**, ***Eloisa Sardella***, CNR-IMIP, Italy **INVITED**

Plasma processing has become a most powerful and versatile tool for surface functionalization of porous materials in biomedical field.

Non equilibrium plasmas have many advantages over wet chemistry approaches: they are highly eco-friendly, have high potentialities in developing surfaces with peculiar characteristics, are capable to be part of in-line material processing and most importantly, can be applied to any material. Consequently, it has opened many new opportunities for investigation of surface modification in various fields like tissue and organ regeneration and biosensing. In this talk, we shall give a brief review on the recent developments of plasma processing of porous materials. We shall describe our experience on non-equilibrium plasmas to modify materials of biomedical interest like: scaffolds for tissue engineering and 3D carbon nanotubes carpets for bio-sensing. This research is aimed to gain new insights on the potentialities of plasma processing of biomedical materials. This work is encouraged by a deep characterization of material's surface and investigation of the material/ bio-environment interface.

3:00pm **SM+AS+BI+PS-ThA3 Advantages of Plasma Polymerized Surfaces for Cell Sheet Engineering over Other Deposition Techniques**, ***Heather Canavan****, M.A. Cooperstein,* University of New Mexico*, B. Bluestein,* University of Washington*, J.A. Reed*, University of New Mexico **INVITED**

Poly(N-isopropyl acrylamide) (pNIPAM) undergoes a conformation change in a physiologically relevant temperature range: it is relatively hydrophobic above its lower critical solution temperature (LCST, ~32oC), and mammalian cells are easily cultured on pNIPAM-grafted surfaces. When the temperature is lowered below the LCST, the polymer's chains rapidly hydrate, and cells detach as intact sheets capable of being used to engineer tissues ("cell sheet engineering"). This behavior has led to a great deal of interest from the bioengineering community, resulting in a variety of film deposition methods, substrate storage techniques, and cell release methods. Unfortunately, this has also resulted in widely varying responses (e.g., % of cells released, biocompatibility and stability of surfaces, etc.) from the resulting cell sheets. In this work, we present a comprehensive comparison of the surface chemistry, biocompatibility, and effect on reversible cell adhesion that results from pNIPAM substrates fabricated using the most common polymerization (free radical and plasma polymerization) and deposition (spin coating and plasma polymerization) techniques. The relative biocompatibility of different mammalian cells (e.g., endothelial, epithelial, smooth muscle, and fibroblasts) was evaluated using appropriate cytotoxicity tests (MTS, Live/Dead, plating efficiency). The pNIPAM-coated surfaces were evaluated for their thermoresponse and surface chemistry using X-ray photoelectron spectroscopy and goniometry. We find that plasma polymerized NIPAM substrates (ppNIPAM) are more stable under a variety of storage conditions prior to their use. Furthermore, when used for cell culture, ppNIPAM films exhibit no cytotoxicity toward any of the cell types tested and yield excellent cell detachment (~85%), which is an important consideration for their ultimate use in engineered tissues.

4:00pm **SM+AS+BI+PS-ThA6 Biofunctionalization of Surfaces by Energetic Ion Implantation: Fundamentals and Recent Progress on Applications**, ***Marcela Bilek***, *A. Kondyurin, E. Kosobrodova, G. Yeo,* University of Sydney, Australia, *S. Wise,* Heart Research Institute, Australia, *N.J. Nosworthy, C.G. dos Remedios, A.S. Weiss, D.R. McKenzie*, University of Sydney, Australia **INVITED**

Despite major research efforts in the field of biomaterials, rejection, severe immune responses, scar tissue and poor integration continue to seriously limit the performance of today's implantable biomedical devices. Implantable biomaterials that interact with their host via an interfacial layer of active biomolecules to direct a desired cellular response to the implant would represent a major leap forward. Another, perhaps equally revolutionary, development that is on the biomedical horizon is the introduction of cost-effective microarrays for fast, highly multiplexed screening for biomarkers on cell membranes and in a variety of analyte solutions.

Both of these advances will rely on the availability of methods to strongly attach biomolecules to surfaces whilst retaining their biological activity. Radicals embedded in nanoscale carbon rich surface layers by energetic ion bombardment can covalently immobilize bioactive proteins [*Proc. Nat. Acad. Sci* **108**(35) pp.14405-14410 (2011)] onto the surfaces of a wide range of materials, including polymers, metals, semiconductors and ceramics . This new approach delivers the strength and stability of covalent coupling without the need for chemical linker molecules and multi-step wet chemistry. Immobilization occurs in a single step directly from solution and the hydrophilic nature of the surface ensures that the bioactive 3D shapes of the protein molecules are minimally disturbed.

This presentation will describe recently developed approaches that use energetic ions extracted from plasma to facilitate simple, one-step covalent surface immobilization of bioactive molecules. A kinetic theory model of the biomolecule immobilization process via reactions with long-lived, mobile, surface-embedded radicals and supporting experimental data will be presented. Progress on applications of this technology to create antibody microarrays for highly multiplexed, simple analysis of cell surface markers and to engineer bioactive surfaces for implantable biomedical devices will be reviewed.

4:40pm **SM+AS+BI+PS-ThA8 Three-Dimensional Biopolymeric Scaffold Surface Modification Using Plasma Enhanced Chemical Vapor Deposition: The Effect of Functionality and Wettability on Cell and Bacterial Attachment**, ***Morgan Hawker***, *A. Pegalajar-Jurado, E.R. Fisher*, Colorado State University

Three-dimensional (3D) bioresorbable polymeric materials, such as porous scaffolds made of poly(ε-caprolactone) (PCL), have desirable bulk properties for tissue engineering, wound healing, and controlled-release drug delivery applications. However, the surface properties (e.g., chemical functionality and wettability) are often undesirable for certain biomedical applications. Therefore, the ability to fabricate 3D materials with ideal bulk properties and customizable surface properties is a critical aspect of biomaterial development. Here, we demonstrate the deposition of conformal films throughout the 3D porous scaffold network using plasma enhanced chemical vapor deposition (PECVD). Resulting film properties can be tailored by using different precursor species. Octofluoropropane (C_3F_8) and hexafluoropropylene oxide (HFPO) precursors were chosen as model hydrophobic film PECVD systems, whereas a copolymerization system consisting of allylamine/allyl alcohol (allylNH/allylOH) precursors was chosen as a model hydrophilic, nitrogen containing PECVD system. To ensure the efficiency and reproducibility of the treatments, both the exterior and interior of the plasma treated scaffolds were characterized using contact angle goniometry, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM) to assess changes in wettability, chemical functionality, and scaffold architecture in comparison to untreated scaffolds. C_3F_8 and HFPO PECVD on scaffolds resulted in fluorocarbon films on the exterior of the scaffold, and the extent of deposition throughout the scaffold's 3D structure was controlled by treatment time. The nitrogen content of the allylNH/allylOH films was tailored by changing the feed gas composition of the copolymerized films. After surface modifications, modified PCL scaffold surface interactions with cells and bacteria were assessed to confirm the relevance of these coatings for the biomedical field. We also explored the effect of different plasma treatments on cell adhesion/proliferation using both human dermal fibroblasts and endothelial cells, bacterial attachment, and biofilm formation using *Escherichia coli*.

5:00pm **SM+AS+BI+PS-ThA9 Plasma Polymerized Bandages for Wound Healing**, ***Jason Whittle***, *L.E. Smith, T.L. Fernandez*, University of South Australia

Wound healing is a multi-billion dollar drain on healthcare systems around the work. This is particularly true in developed countries as they deal with aging populations and conditions such as vascular disease and diabetes. More than 30% of the costs associated with treating diabetes can be attributed to management of chronic wounds. Dressings for the clinical management of wounds are constantly evolving to provide antimicrobial environments and optimal gas exchange, pH and hydration to facilitate wound healing. Ideally, the next generation of wound dressings will also provide a favourable surface for cell attachment, proliferation and migration to further promote the healing process. A number of approaches have been developed for healing chronic wounds, many of which involve culturing of explanted cells, or donor cells, and returning them to the wound site. In this paper, we have used plasma polymerisation to develop surfaces which influence the migration rate of primary cells (keratinocytes, fibroblasts and endothelial cells). A pro-migratory surface will enable cell transport into the wound bed. Earlier workers have concentrated on cell attachment as a key measurement of clinical potential, but we have observed that cell mobility exhibits a preference for different surface chemistry to attachment, and this preference depends on cell type. We show how plasma polymerization can be used to produce surfaces with controllable chemistry, and explore the effect of changing surface chemistry on the migration rate of primary fibroblasts and keratinocytes in vitro. We also investigate the effect of these surfaces on wound closure rate using an in-vitro wounding model based on an engineered skin composite. We also explore the application of plasma polymerized pro-migratory surfaces to electrospun scaffolds for use with deeper wounds.

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 (ΔJ = 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)

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[3] F. D. Natterer, F. Patthey, H. Brune, *arXiv*:1403.1312 (2014)

[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].

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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.

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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.

Applied Surface Science
Room: Hall D - Session AS-ThP

Applied Surface Science Poster Session

AS-ThP1 Formation of Pt, Rh, and Pd Nanoclusters on a Graphene Moire Pattern on Cu(111)*, Esin Soy*, *Z. Liang, M. Trenary*, University of Illinois at Chicago

Formation and growth of Pt, Rh, and Pd nanoclusters on a graphene covered metal substrate has been investigated by ultrahigh vacuum scanning tunneling microscopy (UHV-STM). For this purpose a graphene film was formed on the Cu (111) surface by the decomposition of ethylene at high temperatures. According to our results, isolated graphene islands were successfully grown on the Cu surface with different periodicities. Different rotational domains were observed as a result of weakly coupled Cu and graphene caused by the low C solubility in Cu. The most prevalent moire patterns have periodicity of 2.2, 4 and 6.6 nm with rotational angles of 0° and 1.4°, and 37°. Subsequently, nanoclusters were formed at room temperature on the template of a graphene moire pattern formed on Cu (111) surface. As confirmed by the height and size profiles, Rh and Pt clusters display similar planar structures with an average height of about 0.4 nm and average diameter of about 10 nm. The size and distribution of the metal clusters on the two types of Moirés seem to be different. The clusters on the smaller Moiré pattern show a narrow size distribution in both diameter and height. Additionally, these nanoclusters are found to be relatively stable and only undergo agglomeration at relatively high temperatures. These results demonstrate that the metal-C and metal-metal interactions may play a significant role in the cluster formation and it is possible to fabricate finely dispersed metal nanoclusters on the moire structure of graphene covered Cu (111).

AS-ThP2 Valence Band Offsets of Two Rare Earth Oxides on $Al_xGa_{1-x}N$ ($0\leq x\leq 0.67$) as Measured by Photoelectron Spectroscopy*, Michael Brumbach*, *A. Allerman, D. Wheeler, S. Atcitty, J. Ihlefeld*, Sandia National Laboratories

Preparation of high quality gate oxides on wide bandgap semiconductors is a challenge for realizing efficient high performance devices. For GaN electronics there are a limited number of compatible oxides that have a sufficiently large bandgap to minimize electrical leakage. In this work, reactive molecular beam epitaxy was used to deposit rare earth oxides, Gd_2O_3 and La_2O_3, on GaN substrates. For Gd_2O_3, the valence band offset was tuned by altering the composition of the $Al_xGa_{1-x}N$ substrate. Thin films were characterized using reflection high-energy electron and X-ray diffraction and valence band offsets were determined via X-ray photoelectron spectroscopy.

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

AS-ThP3 Surface Electronics of Individual Si-doped GaN Wires Studied by Synchrotron-Radiation XPEEM Spectromicroscopy*, Olivier Renault*, *N. Chevalier, J.W. Morin*, CEA-LETI, France

Heavily Si-doped GaN wires are at the basis of innovative LEDs used in advanced solid-sate lightning. Understanding how silicon incorporation influences the electronic properties and the measured electrical characteristics of recently emerged very high-conductivity GaN wires [1] is of prime importance for future device optimization.

Here, we have implemented photoemission microscopy with synchrotron radiation (XPEEM) [2] and scanning Auger nanoprobe microscopy (SAM) [3] to investigate the incorporation of Si at the surface of individual GaN wires of 2 µm diameter and the local work function. The high-resolution Si2p micro-spectra evidence complex incorporation of Si pointing on intentional (Si substitution in Ga sites) and un-intentional doping (Si substitution in N-vacancies). By combining elemental analysis from SAM and XPEEM core-level results, we can quantitatively discriminate these two contributions to the doping. Next, we have studied the influence of illumination flux on both the work function and Ga3d binding energies, the strong variations of which evidence surface band bending through the surface photovoltage effect.

This work was carried out at the NanoCharacterization Platform (PFNC) of MINATEC.

AS-ThP6 Characterization of Nanostructured Cu-Zn Oxides Used for Photocathodic Water Splitting*, Sankar Raman*, *J.F. Moulder,* Physical Electronics Inc.*, S. Banarjee,* Washington University, St. Louis*, Y. Myung, H. Im, J. Park,* Korea University*, P. Banarjee*, Washington University, St. Louis

Metal alloys can be efficiently exploited, via controlled fabrication steps, to create mechanically robust and adherent, mixed metal oxide films with tunable photoelectrochemical (PEC) properties. Brass, an alloy of Cu and Zn is an inexpensive source of semiconducting Cu_2O, CuO and ZnO, which have all been used separately as photo-cathodes or photo-anodes respectively for solar water splitting. However, thermodynamics and free energy change predicts a prevalence of ZnO formation when brass is oxidized. We have co-fabricated Cu and Zn oxides to form a highly adherent, mixed metal oxide surface and investigated the relationship between structure property and performance in a PEC cell.

Structural and chemical characterization of the oxide layer was accomplished using an SEM and the PHI X-Tool Scanning XPS microprobe. SEM results show the presence of CuO nanowires interspersed with ZnO fibers and high energy resolution XPS provides detailed chemical state information for Cu and Zn on the surface as a function of sample treatment.

This study indicates that the thermal oxidation of metal alloys can lead to formation of highly interspersed, mixed oxide phases forming novel heterojunctions for use as economical and manufacturing-scalable energy harvesting devices.

AS-ThP8 Impact of a Mixed Oxide's Surface Composition and Structure on Its Adsorptive Properties: The Case of the α-$(Fe,Cr)_2O_3$(0001) Surface*, M.A. Henderson,* ***Mark Engelhard***, Pacific Northwest National Laboratory

Characterization of an α-$(Fe_{0.75},Cr_{0.25})_2O_3$(0001) mixed oxide single crystal surface was conducted using x-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), low energy electron diffraction (LEED) and temperature programmed desorption (TPD). After sputter/anneal cleaning in ultra-high vacuum (UHV), the mixed oxide surface became terminated with a magnetite-(111) structure based on the presence of (2x2) spots in LEED and Fe^{2+} in XPS. The composition of the surface was close to that of M_3O_4 based on XPS, with the metal (M) content of $Fe^{2+/3+}$ and Cr^{3+} being close to 1.4:1, despite the fact that the film's bulk was 3:1 with respect to the metal cations. The enrichment of the surface with Cr was not altered by high temperature oxidation in UHV, but could be returned to that of the bulk film composition by exposure to the ambient. Adsorption of various probe molecules (NO, O_2, CO_2 and H_2O) was used to identify the active cation sites present in the $(Fe,Cr)_3O_4$(111) terminated surface. Although XPS and SIMS both indicated that the near-surface region was enriched in Cr^{3+}, no adsorption states typically associated with Cr^{3+} sites on a -Cr_2O_3 single crystal surfaces were detected. Instead, the TPD behaviors of O_2 and CO_2 pointed toward the main active sites being Fe^{2+} and Fe^{3+}, with O_2 preferentially adsorbing at the former and CO_2 at the latter. NO was observed to bind at both Fe^{2+} and Fe^{3+} sites, and H_2O TPD looked nearly identical to that for H_2O on the Fe_3O_4(111) surface. Competition for adsorption sites between coadsorbed combinations of CO_2, O_2, H_2O and NO corroborated these assignments. These results indicate that the surface composition of a mixed oxide can vary significantly from its bulk composition depending on the treatment conditions. Even then, the surface composition does not necessarily provide direct insight into the active adsorption sites. In the case of the $(Fe,Cr)_3O_4$(111) termination of the α-$(Fe_{0.75},Cr_{0.25})_2O_3$(0001) surface, Cr^{3+} cations in the near-surface region appear to be fully coordinated and unavailable for adsorbing molecules.

AS-ThP9 Analysis of Metal Particles by Proximal Excitation of Al and Mgkα X-rays*, C.F. Mallinson,* ***James Castle***, University of Surrey, UK

In preliminary work [1] we have shown that use of an aluminium substrate to support a distribution of copper particles enables their characteristic photoelectrons to be observed within the Auger electron spectrum generated by an incident electron beam. This observation raises the possibility of the use of chemical shifts and the corresponding Auger parameter to identify the chemical states present on the surface of individual sub-micrometer particles within a mixture. In this context, the technique has an advantage in that, unlike conventional Auger electron spectroscopy, the electron beam does not dwell on the particle but on the substrate adjacent to it. Given the importance, for both medical and toxicological reasons, of the surface composition of such particles we have continued to explore the potential of this development.

In this contribution, we show that proximal excitation of x-rays is equally successful with magnesium substrates: In some regions of the XP spectrum the much larger Auger peaks generated by the electron beam can cause inconvenient clustering of Auger and photoelectron peaks. As in conventional XPS, the ability to switch between Al and Mg sources is useful in such situations. In this context, we have extended the studies to iron and nickel particles where we show that use of Al or Mg substrates, as necessary, can make a contribution to clear identification of individual components in the Fe and Ni 2p peaks.

For this development in electron spectroscopy to achieve its full potential it is necessary to optimise the beam conditions used to generate the local x-ray to give good selectivity of a given particle. Measurements made in support of this will be given. Of greater concern is a possible problem of local heating associated with x-ray generation. We continue to explore this problem and report some progress in minimising heating of the particle whilst maintaining the particle selectivity that is central to this exciting development.

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AS-ThP10 XPS Sputter Depth Profiling of Organometallic Multilayer Materials Using Massive Argon Cluster Ions, ***Simon Hutton***, Kratos Analytical Limited, UK, *T. Bendikov,* Weizmann Institute of Science, Israel, *W. Boxford, SC. Page, J.D.P. Counsell*, Kratos Analytical Limited, UK

Thin polymer films are found in an enormous range of devices and have many applications from use in semi-conductors, displays and solar cells to corrosion protection and packaging. New ion sources such as the multi-mode Ar gas cluster ion source (GCIS) have revolutionised the study of such organic thin films by depth profiling with techniques such as X-ray photoelectron spectroscopy (XPS). As reported elsewhere the chemical composition of organic thin films may now be determined as a function of depth by a combination of XPS analysis and etching using massive Ar ions.

In this study we present results from XPS gas cluster depth profiling of multi-layer organometallic thin films. The multi-layer structures are formed by sequential immersion of a pyridine-terminated template layer on silicon or ITO-coated glass substrates.

AS-ThP11 XPS of Liquids: Chemical Bonding in Ionic Liquids and on Tribo-Films Formed on Cast Iron, ***Harry Meyer***, *J. Qu, H. Luo, W. Barnhill*, Oak Ridge National Laboratory

Parasitic friction in internal combustion engines accounts for 10-15% of the nearly 7 billion barrels of oil consumed by cars and trucks in the United States. Recently a new group of oil-miscible ionic liquids has been developed as next-generation lubricant additives. Among the many positive attributes of these IL-additives are thermal stability, excellent wettability, non-corrosive, and most importantly, they possess effective anti-scuffing/anti-wear and friction reduction characteristics. Since the idea of using ionic liquids (ILs) as lubricants was raised in 2001, many studies have been conducted in this area and results have demonstrated superior lubricating performance for a variety of ILs. It is widely believed that a protective tribo-boundary film is formed on the contact area by tribochemical reactions between the metal surface and the IL during the wear process and, as a result, reduces friction and wear. However, the study of this critical boundary film in the literature has been limited to two-dimensional topography examination and chemical analysis from the top surface. Several ionic liquids have been evaluated in both bench and engine tests at ORNL and have shown superior wear protection compared to conventional anti-wear additives. In this poster, two IL ([N888H][DEHP] and [P8888][DEHP]) have been used in scuff tests of cast iron samples (pin-on-disk arrangement) and are compared with zinc dialkyldithiophosphate (ZDDP), the most common anti-wear additive. X-ray photoelectron spectroscopy (XPS) was first used to examine chemical bonding in the ionic liquids and the ZDDP in their *liquid state*. This is possible due to the extremely low vapor pressure exhibited by these materials (including ZDDP). The scuff tests produce tribo-films on the cast iron samples. XPS depth profiling is used to determine the composition as a function of depth for these tribo-films. Chemical bonding within the tribo-film is compared and contrasted to the photoemission results obtained on the liquid forms of the IL's and ZDDP.

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AS-ThP12 X-ray Photoelectron Spectroscopy for Electronic Structure and Valence Information, *R.G. White,* Thermo Fisher Scientific, UK, ***Thomas Levesque***, Thermo Fisher Scientific

X-ray Photoelectron Spectroscopy (XPS) is well known for its surface specificity and chemical selectivity. By studying the small binding energy shifts of core level spectra, the analyst may identify the chemical bonding environments of elements present in the surface. When electronic structure or valence information is required, however, many analysts will turn to Ultraviolet Photoelectron Spectroscopy (UPS). There have been many publications in the literature which demonstrate that XPS can also provide electronic and valence information, ranging from work function measurements to valence bonding information.

This work demonstrates the utility of XPS for such measurements and compares results from the same sample set using the complementary techniques of XPS and UPS.

AS-ThP13 Mapping Chemical and Mechanical Property Degradation in PV Modules, ***Katherine Stika***, *C.S. Westphal,* DuPont Central Research and Development, *J. Kapur,* DuPont Packaging & Industrial Polymers, *R.G. Raty, J. Li,* DuPont Central Research and Development, *J. Kopchick, W. Gambogi, B. Hamzavytehrany, A. Bradley,* DuPont Photovoltaic Solutions, *J.R. Marsh, B. Foltz*, DuPont Central Research and Development

An understanding of material interactions and degradation pathways in both fielded modules and modules used for accelerated testing is important for photovoltaic (PV) materials specification. As part of the effort to build this understanding, a suite of destructive and non-destructive testing protocols has been developed to compare material performance and reliability under the stresses of different service environments.

This presentation will describe our recent experience mapping the physical and chemical changes observed in degraded PV modules. Examples will include: a) the application of Laser Ablation–Inductively Coupled Plasma–Mass Spec (LA-ICP-MS) for the study of ion migration pathways in encapsulants after PID (Potential Induced Degradation); b) Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) to follow chemical changes in cells extracted from modules following PID and Damp Heat exposure; and c) NanoHardness testing (NHT) to map mechanical property differences in backsheet structures removed from PV modules after field exposure.

AS-ThP14 Surface and Interface Studies of Flexible Front Sheets for PV Modules, ***Lei Zhang***, *N.J. Glassmaker, B.B. Sauer*, DuPont Central Research and Development

To develop the next generation flexible front sheets for photovoltaic (PV) modules, FEP, a tetrafluoroethylene/TFE copolymer with ~10wt% hexafluoro propylene, has shown great promise due to its low refractive index and superior properties in light transmission. The chemical and photochemical inertness of FEP make it an ideal candidate for PV front sheets; FEP is expected to produce approximately ~1.5% to ~5% improvement in module power output over incumbent glass or poly(co-ethylene-TFE) (ETFE) front sheets.

Because FEP is a per-fluorinated polymer, the grand challenge in the development process is to achieve good adhesion between the FEP film and the underlying poly(co-ethylene-vinyl acetate) (EVA) encapsulant layer. The adhesion of glass and ETFE to EVA has been demonstrated to be durable to environmental effects. However, untreated FEP film has poor adhesion to EVA, especially after accelerated weathering test conditions at elevated temperature and humidity. In order to exploit the advantages that FEP can offer for improved module efficiency, we have developed a multi-step treatment process to modify FEP surfaces for enhanced adhesion of FEP to EVA. Integrated analytical techniques including XPS, contact angle, SEM, and others were applied to characterize the complex surfaces and interfaces of the modified fluoropolymer surfaces. These analytical results have enabled us to better understand the treatment induced functionality on the FEP surfaces, especially the possible mechanism and the locus of failure at the FEP-EVA interface. This presentation will focus on the studies of the modified FEP-EVA surfaces/interfaces and their correlation with adhesion performance.

AS-ThP15 Multi-technique Surface Analysis of Catalytic Systems with XPS, ISS and UPS, ***Bill Sgammato***, Thermo Fisher Scientific, UK

Characterization of catalytic systems benefits from analysis with multiple surface analysis techniques. X-ray Photoelectron Spectroscopy (XPS), for example, is the ideal technique for identifying different chemical species present within the top 10nm of a catalyst surface, but if the elemental composition of the top monolayer is to be investigated then Ion Scattering Spectroscopy (ISS) is the preferred analytical technique. Additionally, if the surface electronic structure can be analyzed, using Ultraviolet Photoelectron Spectroscopy (UPS), then it may be possible to correlate catalytic activity with electronic structure enabling the analyst to identify the chemical species and active sites responsible for catalytic reactions.

This work demonstrates how a single, multi-technique surface analysis system can be used to comprehensively characterize a catalytic system. XPS, ISS and UPS data is presented.

AS-ThP16 Multifunctional Ultra-High Vacuum Apparatus for Studies of the Interactions of Chemical Warfare Agents on Complex Surfaces, ***Wesley Gordon***, U. S. Army Edgewood Chemical Biological Center, *E.M. Durke,* Excet, Inc.*, A.R. Wilmsmeyer,* Augustana College*, J.R. Morris*, Virginia Tech

A fundamental understanding of the surface chemistry of chemical warfare agents is needed to fully understand the interaction of these toxic molecules with militarily relevant materials. Knowledge of the surface chemistry of agents can be applied to the creation of next generation decontaminants, reactive coatings, and protective materials for the warfighter. Here, we describe a multi-functional ultra-high vacuum instrument for conducting comprehensive studies of the adsorption, desorption, and surface chemistry of chemical warfare agents on model and militarily relevant surfaces. The system applies reflection-absorption infrared spectroscopy, x-ray photoelectron spectroscopy, and mass spectrometry to study adsorption and surface reactions of chemical warfare agents. Several novel components have been developed to address the unique safety and dosing issues that accompany the research of these toxic, often very low vapor pressure, compounds. Equipment and methods applied in order to safely work with chemical warfare agents will be detailed.

AS-ThP17 A New Transfer Vessel to Facillitate the Characterization of Air-Sensitive Materials, ***Richard White****, T.S. Nunney,* Thermo Fisher Scientific, UK*, H.M. Meyer*, Oak Ridge National Laboratory

Analysing key components of technologically significant devices such as OLED displays, Li-ion batteries and catalyst materials can present challenges to the surface analysts. Amongst the most critical issue is the air sensitivity of these materials. Small amounts of oxygen or water vapour can cause radical changes in the material, ultimately affecting the analysis results and leading to uncertainty in the validity of any conclusions drawn.

Transfer from the preparation environment to the instrument requires the samples to be loaded into a container that can be unloaded into vacuum in the analysis instrument without exposure to the ambient atmosphere . In this presentation we will show results obtained using a new transfer vessel, designed to make the introduction of samples into the vacuum system more automated. Data has been collected from samples covering a range of application areas in order to validate the system, and this will be used to illustrate the benefits of the design.

AS-ThP18 Large-Area Secondary Ion Mapping: An Essential Component of Industrial Problem-Solving, ***Kathryn Lloyd****, J.R. Marsh*, DuPont Corporate Center for Analytical Sciences

Secondary Ion Mass Spectrometry (SIMS), carried out with liquid metal primary ion sources and time-of-flight mass analyzers, has long been recognized as a means of obtaining lateral distributions of species at the surface via detection of chemically-specific molecular ions. As efforts continue to routinely achieve sub-micron lateral resolution from organic and electrically-insulating samples, it is worth noting that the technique easily lends itself to large-area (millimeters to centimeters) chemical mapping. This capability fills an important niche in the chemical mapping “toolbox” and is relevant to many industrial surface-related problems.

For small-area (less than 500x500 μ m^2) mapping, the primary ion beam optics are (usually randomly) rastered across a pixel array spanning the area of interest, and secondary ion spectral data is collected at each pixel. In the simplest implementation of large-area mapping, the sample stage is moved in regular (essentially large pixel) intervals under an optically-stationary primary ion beam. A more optimal approach is to combine both small-area ion beam rastering with stage rastering in a so-called “patch” configuration.

These large-area mapping acquisitions typically take 30 minutes. Coupled with multivariate analysis, they provide a chemical view of the surface not easily obtainable from other techniques. Examples shown will include optimization of anti-stat coating, understanding fabric color streaking, and assessment of printing uniformity.

AS-ThP19 *In Situ* Ar Plasma Cleaning of Samples Prior to Surface Analysis, ***Vincent Smentkowski****, H. Piao,* General Electric Global Research Center, *C.A. Moore*, XEI Scientific

The surface of as received samples is often contaminated with adsorbed layers of hydrocarbons. These surface contaminants can attenuate or mask underlying species of interest, inhibiting or compromising accurate analysis. *In-situ* ion beam sputtering is often used to remove the outer layer of a sample surface and thus remove contaminants, however this erosion process is inherently destructive and can alter the surface of interest. Moreover there are also many materials that can not be cleaned using monoatomic ion beam sputtering as the material(s) may decompose and deposit a layer of fragments onto the outer surface of the material to be analyzed. Recently gas cluster ion beams (GCIB) have been developed[1,2], which allows for depth profile analysis of organic layers with minimal degradation[3] (and references therein). GCIBs have also been used for low damage surface cleaning[4,5,6]. A non line-of-sight protocol which is able to clean large (mm or greater) areas is desired. We recently demonstrated that ambient air plasma processing can be used to clean the outer surface of samples[7], however ambient air plasma treatment can result in oxidation of the material. In this presentation we report our first attempts at *in-situ* plasma cleaning of samples using Ar prior to XPS and ToF-SIMS analysis. We compare Ar plasma cleaning with air plasma cleaning, and report key findings.

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AS-ThP20 Discrete Distribution Profile Model for Characterization of Ultra-Thin Surface Films, ***Tatyana Bendikov****, T. Toledano, H. Cohen*, Weizmann Institute of Science, Israel

Accurate characterization of ultra-thin surface films is a basic requirement for the successful development of the electronic devices. For example, electrical transport measurements in molecular electronics, often consisting of ultra-thin films, are extremely sensitive to the quality of the films and their associated interfaces. As an experimental technique, X-ray Photoelectron Spectroscopy (XPS) is uniquely suited for the direct characterization of thin films in terms of layer thicknesses, elemental composition and, frequently, the depth-distribution profile of elements across the film. However, interpretation of the raw experimental data requires a reliable theoretical modeling of the photoelectron attenuation; a mechanism that is usually addressed by considering a continuum medium with a phenomenological attenuation parameter. Such models impose severe limitations when self-assembled molecular layers (SAMs) are to be analyzed. In SAMs studies, calculations based on a Discrete Distribution Profile (DDP) are necessary for a proper accounting of atoms situated at the specific locations along the molecular backbone.

In this work, 1-undecane, 11-chloro monolayer deposited on Si substrate was used as a model system. XPS intensities of carbon, chlorine, oxygen and silicon were measured and their components (C_{Cl}, C_{Si}, Si_{ox}, Si_C) were quantified using curve fitting analysis. The intensity ratios (C_{tot}/Cl, C_{tot}/C_{Cl}, C_{tot}/C_{Si}, C_{tot}/Si_C, C_{Si}/Si_C) were then compared to DDP calculated ratios, yielding excellent agreement between experimental and calculated values. The detailed agreement points to the high quality of the studied layers and, more generally, supports the validity of the DDP model as a tool for thin films characterization.

AS-ThP24 Co-solvent Enhanced Zinc Oxysulfide Buffer Layers in Kesterite Cu2ZnSnSe4 Solar Cells, ***Xerxes Steirer****, R.L. Garris, J. Li,* National Renewable Energy Laboratory*, M. Dzara,* Rochester Institute of Technology*, P.F. Ndione, K. Ramanathan, I. Repins, G. Teeter, C.L. Perkins*, National Renewable Energy Laboratory

Thin film solar cells rely upon the efficient transfer of photocharge from the absorbing photovoltaic material to an external circuit via thin buffer junction layers. Problems such as low fill factor and current loss arise when the electron collecting contact (emitter) exhibits a large positive conduction band discontinuity with the absorber. This study shows evidence for one approach to circumvent this problem by taking advantage of electronic defects prominent with chemical bath deposition (CBD) of buffer layers. X-ray and ultraviolet photoelectron spectroscopy (XPS/UPS) of heterojunctions formed between CZTSe and CBD-ZnOS with two different buffer preparations exhibit clear differences in electronic properties yet we observe no discernable differences in composition. Structure of CBD-ZnOS made using the different preparation methods is measured with grazing incidence X-ray diffraction (GIXRD) and also exhibits no discernable differences in the peak positions or full widths. XPS/UPS derived band energy diagrams are presented for quasi-*in-situ* prepared CZTSe/CBD-ZnOS interfaces with both preparation methods yielding valence band offsets equal to -1.0 eV and conduction band offsets equal to 1.1 eV. However, comparison between water only and a water/dimethyl sulfoxide solvent mixture in device characterization and band offset measurements show increased band bending in accordance with higher n-type carrier density with water as the only solvent. Seemingly incongruous, the more strongly n-type buffer layer performs worse in solar cells and exhibits inflected current-voltage response under one-sun illumination. A proposed electron transport band for these buffer layers that seems to circumvent the large conduction band spike is estimated to have energies about 0.6 eV below the conduction band of the CBD-ZnOS. Hence, these defects appear to enable adequate band-lineup with the low-band gap absorber, CZTSe (E_g = 0.96 eV). These findings suggest that cosolvation approaches may allow for the manipulation of the electronic structure of ZnOS and enable a wider range of electronic applications where larger electron affinities are required.

AS-ThP25 Analysis of Metal Nanoparticles by Auger, XPS and TEM, ***Wayne Jennings***, Case Western Reserve University, *C.V. Bishop,* The Best Mode Company, *J. Cowen,* Case Western Reserve University, *J.S. Hammond, D.F. Paul*, Physical Electronics USA

Nanoparticles of Pd and PdSn are important as catalysts for chemical reactions and metallization of polymeric materials. Metallization applications include nano-circuitry and automotive plating on plastic. Catalytic applications include the Heck and Suzuki reactions and a variety of other coupling reactions (hydrogenation, dehydrogenization and petroleum cracking). A common synthesis route for Pd nanoparticles is reduction of PdCl2 with stannous compounds. The structure and purity of the resulting particles is critical to their performance. TEM has been used to examine PdSn nanoparticles for their compositional structure. For very small particles, EDS and EELS analyses become difficult due to the expanded excitation volume. Surface sensitive methods have utility for effective characterization of materials of this type. This work demonstrates the utility of scanning Auger analysis in characterization of particles of this type that effectively compliments TEM methods.

Fundamentals & Biological, Energy and Environmental Applications of Quartz Crystal Microbalance Focus Topic
Room: Hall D - Session QC+AS+BI+MN-ThP

Fundamentals & Biological, Energy and Environmental Applications of Quartz Crystal Microbalance Poster Session

QC+AS+BI+MN-ThP1 *In Situ* Toxic Nano-Material Sensing Method Using DNA Immobilized Quartz Crystal Microbalance, ***Kuewhan Jang***, *S. Lee, J. You, C. Park, J. Park, S. Na*, Korea University, Republic of Korea

Nano-material has grown from scientific interest to commercial products and there are more than 1600 nano-material products on the market. Among those nano-materials, single-walled carbon nanotube (SWNT) and silver ion have been shown great interest due to their extraordinary properties. Since SWNT and silver ion production capacity increases each year, its contamination to the environment water system will increase in the form of industrial waste. Moreover, toxicity assessment of those materials is required for human health and environmental issue since the toxicity of those materials has been reported. In this study, we propose the in-situ detection of SWNT and silver ion. The detection mechanism is based on the measurement of the resonance frequency shift arisen from the binding on the DNA immobilized quartz crystal microbalance. We are able to detect SWNT and silver ion less than an hour with the detection limit of 100 ng/ml of SWNT and 100 pM of silver ion, respectively. Moreover, the DNA immobilized quartz crystal microbalance enables the detection in real tap water. This work shows the potential of DNA immobilized quartz crystal microbalance as the in-situ toxic nano-material screening tool.

QC+AS+BI+MN-ThP2 Mechanics of Multicontact Interfaces Studied with a QCM, *R. König, S. Hanke, J. Vlachová, D. Johannsmann,* ***Arne Langhoff***, Clausthal University of Technology, Germany

The contact stiffness and the contact strength at interfaces between rough surfaces are of outstanding relevance in many different fields, including mechanical engineering, bio-lubrication, and technical tribology.

Individual sphere-plate contacts have been previously investigated with a QCM and it was found that the contact stiffness can be inferred from the frequency shift, where the latter is positive because contact increases the overall stiffness of the composite resonator. At elevated amplitude of oscillation, the apparent contact stiffness decreases because of partial slip. Partial slip (also: "microslip") describes the situation, where a contact partly sticks and partly slips. Sticking mostly is observed in the center. Slip is found at the edges, where the local stress is large.

The presentation describes the extension of this work to multicontact interfaces as well as the new results which were found with the single contacts . Generally speaking, multicontact interfaces differ from individual contacts by, firstly, a broad distribution of contact size and contact strength and, secondly, by an elastic coupling between neighboring load-bearing asperities.

Different materials (aluminum, PMMA) and different characteristic scales of roughness (all in the range of many microns) were studied. The focus is on polymer surfaces, which where treated with an abrasive paper. A novel geometry, where the resonator is symmetrically loaded with the same type of sample from both sides, has allowed to increase the normal force by a factor of 10, compared to previous experiments.

At small amplitudes, the frequency response of the QCM to a contact with rough PMMA surfaces is similar to the behavior observed with individual sphere-plate contacts. There is an increase in resonance frequency, which can be converted to an interfacial stiffness. Interesting, the contact stiffness observed with MHz excitation was found to much higher than what has been found similar samples with excitation frequencies in the kHz range.

At elevated amplitudes, the behavior is variable. Often one finds partial slip. Occasionally, however, there is a sharp increase in contact stiffness at a certain threshold in amplitude. The bandwidth goes through a maximum at that same amplitude. The behavior is reversible; the threshold is the same for decreasing and increasing amplitude ramps. We tentatively associate the increased apparent stiffness with an oscillation-induced increase in contact area.

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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.

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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).

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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 x 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.

References: 1. N. Hubin, L. Noethe, Science 262 (1993), 1390.

2. L. Yan, X. M. Zhao, G. M. Whitesides, J. Am. Chem. Soc. 120 (1998), 6179.

3. P. Goel, K. Singh, J. P. Singh, RSC Advances 4 (2014),11130.

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.

[1] L. Qu et al., ACS Nano, 4 (2010) 1321.

[2] T. Kondo, S. Casolo, T. Suzuki, T. Shikano, M. Sakurai, Y. Harada, M. Saito, M. Oshima, M. Trioni, G. Tantardini and J. Nakamura, Phys. Rev. B 86 (2012) 035436.

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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[2]. Bruno Dlubak, et al. Nat. phys, 8, 557 (2012)

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[5]. X. He, et al. Nat. Mater. 9, 579 (2010).

[6]. N. Wu, et. al., Phys. Rev. Lett. 106, 17 (2011).

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 1.14×10^{-12} V/ion for Ar^{1+} ions to 1.12×10^{-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.

[1] S. Chadov, X. Qi, J. Kubler, G. H. Fecher, C. Felser, and S. C. Zhang, Nat. Mater. **9**, 541 (2010).

[2] N. P. Butch, P. Syers, K. Kirshenbaum, A. P. Hope, and J. Paglione, Phys. Rev. B **84**, 220504(R) (2011).

[3] W. Wang, Y. Du, G. Xu, X. Zhang, E. Liu, Z. Liu, Y. Shi, J. Chen, G. Wu, and X. Zhang, Scientific Reports **3** (2013).

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.

Thin Film
Room: 307 - Session TF+AS-FrM

Thin Film Characterization
Moderator: Mark Davidson, University of Florida

8:20am **TF+AS-FrM1 Stability of Platinum Silicide Thin Films above 1000°C**, ***Robert Fryer***, *R.W. Meulenberg, G.P. Bernhardt, R.J. Lad*, University of Maine

Stable, electrically conductive thin films are needed as components for sensors and actuators operating in harsh environments at temperatures above 1000°C, such as those found in turbine engines, power plants, and high temperature materials manufacturing. The Pt-Si thin film system has been extensively studied in the microelectronics industry but the focus has been on film characteristics below 800°C. In this work, Pt-Si films were grown at varying compositions and deposition temperatures on sapphire and fused silica substrates by electron-beam evaporation of Pt and Si sources in ultra-high vacuum (<10^{-9} Torr); the chemical and thermal stability of the Pt-Si films, both in air and in vacuum, at temperatures between 1000–1200°C were studied. X-ray diffraction (XRD) of as-deposited films indicates the formation of a polycrystalline tetragonal-Pt_2Si phase for Pt-rich film compositions, an orthorhombic-PtSi phase near the $Pt_{50}Si_{50}$ composition, and an amorphous film for Si-rich film compositions. The electrical conductivities of these films, measured by a 4-point probe, are in the range of $1x10^6$ to $5x10^4$ S/m, with the conductivity decreasing at higher Si content. Annealing in vacuum at 1000°C causes grain growth and a marked increase in film conductivities. During annealing in air at 1000°C, film oxidation occurs leading to the formation of Pt-oxide phases coinciding with the Pt-Si phases, but only a ~3-fold decrease in film conductivities. After four hours at 1200°C in air, the Pt-Si films become insulating due to morphological roughening and formation of highly faceted Pt (111) and (200) nanocrystallites coexisting in a SiO_2 matrix. Scanning electron microscopy (SEM) revealed that the use of a 50 nm capping layer of amorphous Al_2O_3, grown by atomic layer deposition (ALD) on top of the

Pt-Si films, helps retard oxidation thereby preserving film conductivities in the 10^6-10^4 S/m range and leading to greater film stability as a function of annealing time at 1000°C in air.

8:40am **TF+AS-FrM2 Bulge Testing for Mechanical Characterization of sp^2/sp^3 Carbon Thin Films**, ***Joseph Rowley****, R.C. Davis, R.R. Vanfleet, N. Boyer,* Brigham Young University*, S. Liddiard, M. Harker,* Moxtek, Inc*, L. Pei*, Brigham Young University

Bulge testing is a technique employed to measure material properties of thin films. Pressurized gas is applied to one side of a film and it's subsequent deformation measured. In many cases, thin films are fragile and therefore difficult to handle. Bulge testing has the advantage of requiring much less handling than other methods, resulting in fewer samples lost to error or accident. Carbon membranes have a wide range of characteristics, depending on their bonding and nano-structure. They can have very desirable properties such as: being chemically inert, high wear resistance and low friction, and high hardness and/or strength. In this work, reactively sputtered sp^2 carbon, diamondlike carbon from a pulsed laser deposition process, and a carbon nanotube reinforced polymer were characterized. PEELS and Raman Spectroscopy were used to determine sp^3/sp^2 ratios and density, CHN testing was used to determine hydrogen content, measuring the resonant frequency was a measure to check stiffness, and bulge testing was used to obtain the Young's Modulus and tensile strength.

9:00am **TF+AS-FrM3 Time Dependent Dielectric Breakdown Measurements of Porous Organosilicate Glass using Mercury and Solid Metal Probes**, ***Dongfei Pei****,* University of Wisconsin-Madison*, M.T. Nichols,* Applied Materials*, S.W. King, J.M. Clarke,* Intel Corporation*, Y. Nishi,* Stanford University*, J.L. Shohet*, University of Wisconsin-Madison

Time-dependent dielectric breakdown (TDDB) is a major concern for low-k organosilicate (SiCOH) dielectrics. To examine the effect of plasma exposure on TDDB degradation, both the time-to-failure (TTF) and charge-to-failure (CTF) measurements [1] were made on porous SiCOH before and after exposure to Ar plasma. Significant discrepancies between mercury and solid-metal probes are observed. With XPS measurement data, a significant amount of mercury was found to have drifted into the porous SiCOH film. This implies that the electrical measurement of porous low-k material under mercury probe may be inaccurate due to this mercury drift effect.

This work was supported by the Semiconductor Research Corporation under Contract 2012-KJ-2359 and by the National Science Foundation under Grant CBET-1066231.

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[1] M. T. Nichols, H. Sinha, C. A. Wiltbank, G. A. Antonelli, Y. Nishi, and J. L. Shohet, Appl. Phys. Lett **100**, 112905 (2012)

9:20am **TF+AS-FrM4 The Equivalent Width as a Figure of Merit for XPS Narrow Scans**, ***Matthew Linford****, B. Singh,* Brigham Young University*, J. Terry*, Illinois Institute of Technology

X-ray Photoelectron Spectroscopy (XPS) is a widely used surface analytical tool that provides information about the near surface regions of materials. In particular, chemical state information is often obtained from peak fitting XPS narrow scans. And while indispensable for XPS data analysis, peak fitting can be a fairly subjective exercise. Herein we introduce the use of the equivalent width (EW) as an additional and less subjective figure of merit for XPS narrow scans. The EW_{XPS} is simply defined as the area of a narrow scan divided by the height of the maximum of its peak envelope. To limit any ambiguity in EW_{XPS} for a series of spectra, we may also list the peak position of the maximum of the envelope (PE_{max}). We provide and discuss four examples that demonstrate the use of these parameters including (i) four C 1s narrow scans of ozone-treated carbon nanotubes (EW_{XPS} ~ 2.11 – 2.16 eV for a Shirley background, and up to 2.88 eV for no background, PE_{max} ~ 284.4 – 284.5 eV), (ii) a series of silicon wafers with different oxide thicknesses (EW_{XPS} ~ 1.5 – 2.8 eV, PE_{max} ~ 99 – 103 eV), (iii) hydrogen-terminated silicon before and after derivatization with pentyl groups, and after annealing of the pentyl-modified material (EW_{XPS} ~ 0.7 – 1.0 eV, PE_{max} ~ 25.9 – 26.1 eV), and (iv) five C 1s narrow scans of nanodiamond samples, where three of the spectra showed charging (EW_{XPS} ~ 2.6 – 4.9 eV, PE_{max} ~ 272.7 – 293.9 eV). In this final example, EW_{XPS} was plotted against PE_{max} to identify the region corresponding to the materials that showed the least charging. EW_{XPS} and PE_{max} appear to correlate with the expected chemistries of all the systems studied. We calculate EW_{XPS} using a Shirley baseline and with no baseline at all. In setting the baseline limits for EW_{XPS}, we consider the derivative of C 1s narrow scans. We also show the application of EW_{XPS} to single, fitted components within a narrow scan. Other width functions are also discussed.

9:40am **TF+AS-FrM5 Characterization of Epitaxial Oxides for Electronics, Magnetics, and Photoactivity**, ***Tiffany Kaspar****,* Pacific Northwest National Laboratory **INVITED**

Transition metal oxides offer an incredibly rich variety of properties which can be harnessed for countless applications. Unfortunately, this variety can be a curse as well as a blessing: the myriad oxidation states, crystal structures, and defects which may occur in the bulk and/or on the surface of any given oxide system makes it challenging to draw meaningful structure-property relationships without employing a full suite of materials characterization techniques. To keep the system as simple and well-defined as possible, and to explore materials and compositions not easily attainable by equilibrium techniques, epitaxial deposition of oxide thin films is widely utilized. However, even in these “simple” systems, thorough characterization of the crystallinity and structural defects, oxidation state, stoichiometry and dopants is critical. Unwelcome surprises are often found in nominally “good” material when one takes the time to investigate. Our laboratory has explored the electronic, magnetic, and photoactive properties of binary and complex oxides as epitaxial thin films, and several examples illustrating the importance of thorough thin film characterization will be presented. In our work on Cr-doped anatase TiO_2, a candidate dilute magnetic semiconductor (DMS), room temperature ferromagnetism was observed that appeared to depend sensitively on “preparation conditions.” We applied several characterization techniques, particularly x-ray diffraction (XRD) and transmission electron microscopy (TEM), and were able to correlate the presence of structural defects with room temperature ferromagnetic ordering. One of the most widely investigated materials as a potential DMS has been Co-doped ZnO, but the presence of intrinsic ferromagnetism in this system has been widely debated in the literature. We investigated very high quality epitaxial thin films with several x-ray absorption-based characterization techniques (XANES, EXAFS, XLD) to disprove the presence of intrinsic ferromagnetism in nominally defect-free material. In more recent work, we have explored the visible-light photoactivity of hematite Fe_2O_3 doped with Cr or V. XRD, x-ray photoelectron spectroscopy (XPS), scanning TEM (STEM), and XANES/EXAFS have been applied, as well as less widely utilized techniques such as non-Rutherford resonant elastic scattering (RES) to quantitatively measure oxygen stoichiometry non-destructively, and lab-based x-ray photoelectron diffraction (XPD) to elucidate unique surface oxidation features observed by XPS. The structural properties of doped hematite could then be correlated with the bandgap and spectroscopic photoconductivity measurements.

10:40am **TF+AS-FrM8 Low Energy Ion Scattering Data Analysis for Ultra Thin Films using TRBS**, ***Thomas Grehl****, P. Brüner,* ION-TOF GmbH, Germany*, B. Detlefs, E. Nolot, H. Grampeix,* CEA-LETI, France*, E. Steinbauer, P. Bauer,* Johannes Kepler University, Austria*, H.H. Brongersma*, ION-TOF GmbH, Germany

Low Energy Ion Scattering (LEIS) is well known for its extreme surface sensitivity, allowing elemental characterization and quantification of the outermost atomic layer. This makes it a valuable tool for thin film analysis, e.g. to gain insights to the early stages of film growth or determine film closure. Also contamination analysis can be performed, again making use of the high surface sensitivity to assess the surface composition as the basis for subsequent deposition steps.

In addition, distinct information about sub-surface layers is obtained in a non-destructive way, giving information about the depth distribution of elements up to 10 nm. Although the mechanism for this in-depth signal is well understood, a model for the quantification of the data needs to be established.

One way of modeling the data is demonstrated using TRBS [1], a specialized version of TRIM [2] which was optimized for simulating ion scattering. Combining the TRBS data for backscattering of primary ions and an empirical model for the energy dependent reionization probability gives promising results. By fitting the simulation to the measured data conclusions about film composition, thickness and interface quality can be drawn.

This approach will be demonstrated using different thin film examples. One of the sample sets consisting of HfO_2/Al_2O_3 stacks also characterized by AR-XPS, XRR and GIXRF will be discussed in detail. We will show the possibility to determine film thickness variations in the Å range. These measurements can be performed in a few minutes without destroying the sample by sputtering. At the same time, the composition of the outer atomic layer is detected, making the approach well suited for routine analysis of films during or after deposition.

[1] A particularly fast TRIM version for ion backscattering and high energy implantation, Biersack, J.P.; Steinbauer, E.; Bauer, P.; Nucl. Instr. and Meth. in Phys. Res., B61, 1991, 77-82

[2] The Stopping and Range of Ions in Solids; Pergamon, New York, 1985

11:00am **TF+AS-FrM9 Polarization-dependent X-ray Absorption Fine Structure Analysis of TES Pentacene Thin Films**, ***Beatrix Pollakowski***, Physikalisch-Technische Bundesanstalt (PTB), Germany, *J. Wade, JS. Kim,* Imperial College London, UK, *F.A. Castro,* National Physical Laboratory (NPL), UK, *J. Lubeck, R. Unterumsberger,* Physikalisch-Technische Bundesanstalt (PTB), Germany, *A. Zoladek-Lemanczyk,* National Physical Laboratory, UK, *B. Beckhoff*, Physikalisch-Technische Bundesanstalt (PTB), Germany

Research in organic electronics shall open up alleys for many of its promising applications, including promising applications, including: light emitting diodes, photovoltaics, transistors, biosensors and photonic devices. Despite of the diversity of device functionalities, all these applications are based on thin films of organic materials and in each case their performance is critically dependent upon the precise arrangement and packing structure of the organic molecules in thin films. Our research focuses on this fundamental issue, seeking to better understand the relationships between device performance and thin film morphology of organic semiconductors on the molecular scale [1,2].

A set of 6,13-Bis((triethylsilyl)ethynyl)pentacene (TES-PEN) samples has been prepared on a silicon substrate by using a well controlled printing technique.[2] Different substrate shift speeds were used to modify the layer thickness and the crystallinity.

All X-ray based measurements were carried out at the plane grating monochromator PGM beamline for undulator radiation in the laboratory of the Physikalisch-Technische Bundesanstalt PTB at BESSY II, providing tunable radiation of both high photon flux and high spectral purity in the soft x-ray range [3]. Different kinds of X-ray spectrometry (XRS) analyses were employed to determine the chemical binding state, elemental distribution depending on the depth, and lateral mass deposition.

To analyze the chemical binding state of the molecules, the method Near-Edge X-ray

Absorption Fine Structure spectroscopy (NEXAFS) in fluorescence mode has been employed. Varying the angle of incidence in the fluorescence mode the information depth can be tuned to a pre-selectable depth of interest. In addition, the mean penetration depth at large angles of incidence is high enough to analyze even thicker layers of up to a few hundreds of nanometers as is often the case for complex organic materials. For an analysis of the molecular orientation, the angle between the electric field vector and predominant direction of the molecules has to be varied.

Initial measurement sequences exhibit the potential of this X-ray spectrometry method to significantly contribute to the quantitative analysis of organic materials in thin films. In particular, polarization dependent NEXAFS offers a clear discrimination capability for the orientation of the molecules.

[1] S. Wood, J.S. Kim, D.T. James, W.C. Tsoi, C.E. Murphy, and J. S. Kim, J. Chem. Phys. 139, 2013, 064901

[2] D.T. James, J. M. Frost, J. Wade, J. Nelson, J. S. Kim, ACS Nano 7(9), 2013, 7983.

[3] J. Lubeck, B. Beckhoff, R. Fliegauf, I. Holfelder, P. Hönicke, M. Müller, B. Pollakowski, F. Reinhardt, J.

11:20am **TF+AS-FrM10 Surface Induced Phases in Organic Thin Films: Methods of Crystal Structure Solutions**, ***Roland Resel***, *C. Röthel, A. Pichler,* Graz University of Technology, Austria, *I. Salzmann,* Humboldt University, Germany, *R.G. DellaValle, O. Rosconi,* University Bologna, Italy, *T. Dingeman,* Delft University of Technology, Netherlands, *C. Simbrunner*, University Linz, Austria

A large number of organic molecules exhibit polymorphism and a well-known phenomenon are specific crystallographic phases which are present exclusively in thin films. Such crystallographic phases are often denoted as surface induced phases, since the presence of a surface during the crystallisation is of primary importance for their formation. In general, such thin-film polymorphs do not exist as macroscopic free standing single crystals, so that existing methods of crystal structure solution e.g. from single crystal diffraction or powder diffraction does not work. A number of surface induced crystal structures of conjugated molecules are solved during the last years, examples are in relevant molecules for organic electronic applications like pentacene or sexithophene.

Two different methods of structure solution from a thin films will be introduced. Both methods are based on grazing incidence x-ray diffraction. In a first step the crystallographic unit cells and the lattice constants are determined by indexing the diffraction pattern. The evaluation of the molecular packing is based on either rigid body refinement or molecular dynamics simulations. While rigid body refinement is based on test structures and a comparison of the calculated diffraction intensities with the experimental intensities, molecular dynamics work on energy minimisation of the molecular packing. It is found that the approach works best for fully rigid molecules like pentacene or parylene. Good results are also obtained for semi-rigid molecules like ternaphtalene or molecules with flexible side-chains like dioctyl-terthiophene. In both cases the crystallographic unit cell is filled by two molecules. However an increasing number of molecules per unit cell (e.g. four) makes the solution of the surface induced phases difficult. Similarities and differences in the molecular packing between known crystal structures (from single crystal solutions) and surface induced phases will be discussed.

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