Applied Surface Science Division
Room: 13 - Session AS+BI+MI-MoM

Practical Surface Analysis: Getting the Most Out of Your Analysis using Complementary Techniques

Moderators: Mark Engelhard, EMSL, Pacific Northwest National Laboratory, Michaeleen Pacholski, The Dow Chemical Company

8:20am **AS+BI+MI-MoM1 Obtaining Complete Characterisation of Core-shell Nanoparticle Structure and Composition *via* the use of Complementary Techniques**, ***David Cant***, *C. Minelli*, National Physical Laboratory, UK, *K. Sparnacci*, Università degli Studi del Piemonte Orientale, Italy, *W. Unger*, Bundesanstalt für Materialforschung und -prüfung (BAM), Germany, *A. Hermanns*, Bundesanstalt für Materialforschung und -prüfung (BAM), *W.S.M. Werner, H. Kalbe*, TU Wien, Austria, *R. Garcia-Diez, C. Gollwitzer, M. Krumrey*, Physikalisch-Technische Bundesanstalt, Germany, *A.G. Shard*, National Physical Laboratory, UK

Core-shell nanoparticles are commonly used in a variety of applications, including medicine, catalysis, optoelectronics, and others. Accurate identification of core-shell nanoparticle structure and morphology is an important challenge to overcome before such nanoparticles can be effectively utilised. This is not necessarily a trivial obstacle, as no single characterisation technique can accurately identify every possible peculiarity of structure or composition that may exist.

For example, characterisation methods that observe bulk properties, such as differential centrifugal sedimentation (DCS), thermogravimetric analysis (TGA), or techniques based on observation of Brownian motion such as dynamic light scattering (DLS) may be unable to distinguish particles with a standard core-shell morphology from those with the same core and shell masses, but with an uneven shell, or where the core and shell have merged to form a homogenous particle.

Similarly, surface sensitive techniques which analyse a population of particles, such as x-ray photoelectron spectroscopy (XPS) or small angle x-ray scattering (SAXS), may be able to provide information on shell thicknesses in standard core-shell particles and distinguish them from particles with an uneven shell or a homogenous particle, but may have difficulty distinguishing homogeneity from an uneven shell or off-centred core.

Techniques that allow observation of individual particles, such as electron microscopy, may be able to clearly show the structure, but are rarely able to provide any in-depth quantification of the composition. As such it is necessary to use a careful selection of appropriate techniques to fully characterise any given nanoparticle system. To illustrate these issues, two polymeric core-shell nanoparticle systems have been characterised, both consisting of a Hyflon® core coated in varying thicknesses of either PMMA or polystyrene. These systems are nominally very similar, but differ notably in structure. The results from several different characterisation techniques (XPS, SAXS, DCS, TGA, DLS, and SEM.) were compared in order to demonstrate the difference in information provided by each and obtain a full understanding of both types of nanoparticle.

9:00am **AS+BI+MI-MoM3 Correlative Microscopy based on Secondary Ion Mass Spectrometry for High-Resolution High-Sensitivity Nano-Analytics**, ***Tom Wirtz***, *J.-N. Audinot, D.M.F. Dowsett, S. Eswara*, Luxembourg Institute of Science and Technology (LIST), Luxembourg **INVITED**

Development of innovative characterization tools is of paramount importance to advance the frontiers of science and technology in nearly all areas of research. In order to overcome the limitations of individual techniques, correlative microscopy has been recognized as a powerful approach to obtain complementary information about the investigated materials. High-resolution imaging techniques such as Transmission Electron Microscopy (TEM) or Helium Ion Microscopy (HIM) offer excellent spatial resolution. However, the analytical techniques associated with TEM such as Energy Dispersive X-ray spectroscopy (EDX) or Electron Energy-Loss Spectroscopy (EELS) are inadequate for the analysis of (i) isotopes, (ii) trace concentrations (< 0.1 at. % or < 1000 ppm) and (iii) light elements (H, Li, B). Likewise, for the case of HIM, until recently there was no direct possibility to perform elemental mapping because sub-30 keV He$^+$ or Ne$^+$ ion irradiation do not excite X-ray emission. Secondary Ion Mass Spectrometry (SIMS), on the other hand, is an extremely powerful technique for analysing surfaces owing in particular to its excellent sensitivity (detection limits down to the ppb are possible, so that SIMS can be used to detect both major and trace elements), high dynamic range (a same signal can be followed over several orders of magnitude), high mass resolution and ability to differentiate between isotopes.

In order to combine the high spatial resolution of TEM and HIM with the analytical sensitivity of SIMS, we developed integrated TEM-SIMS [1,2] and HIM-SIMS [2-4] instruments. The main advantage of this in-situ correlative approach is its capability to analyse the same area of interest of any sample without need of transferring the sample from one instrument to another one, which would result in a number of artefacts ranging from surface contamination to issues with localizing exactly the same ROIs. Moreover, the integrated approach allows fast and multiple interlacing between the different imaging and analysis modes.

In this talk, we will first introduce the TEM-SIMS and HIM-SIMS instruments and discuss their performance characteristics. We will then present a number of examples taken from various fields of materials science and life science to show the powerful correlative microscopy possibilities enabled by these new in-situ methods.

[1] L. Yedra et al., Sci. Rep. 6, 28705, 2016

[2] T. Wirtz et al., Nanotechnology 26 (2015) 434001

[3] T. Wirtz et al., Helium Ion Microscopy, ed. G. Hlawacek, A. Gölzhäuser, Springer, 2017

[4] P. Gratia et al, J. Am. Chem. Soc. 138 (49) 15821–15824, 2016

9:40am **AS+BI+MI-MoM5 New Insights on Layered Polymer Systems, Polymer Networks and Polymerization in Defined Geometries by Combining Surface Analysis with Depth Profiling using ToF-SIMS and XPS as Analytical Tools**, ***Sven Steinmüller***, Institute for Applied Materials, Karlsruhe Institute of Technology, Germany, *A. Llevot*, Institute of Organic Chemistry, Karlsruhe Institute of Technology, Germany, *D. Moock*, Institute for Applied Materials, Karlsruhe Institute of Technology, Germany, *B. Bitterer*, Institute of Organic Chemistry, Karlsruhe Institute of Technology, Germany, *F. Cavalli*, Institute for Biological Interfaces, Karlsruhe Institute of Technology, Germany, *S. Hurrle*, Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, Germany, *M. Bruns*, Institute for Applied Materials, Karlsruhe Institute of Technology, Germany

Surface analytical characterization of polymers is still a tough topic if precise information are favored. Especially for characterization of stepwise layered systems and for studying reaction rates and composition of network formation or to confirm polymerization within defined geometries a lot of techniques are not sensitive enough to fulfill the desired degree of precision and resolution. Within the recently installed Cooperate Research Center “SFB 1176” at KIT (Molecular Structuring of Soft Matter), a high degree of precision is necessary to qualitatively and quantitatively confirm the defined structures achieved during the polymer syntheses. Here a new surface analysis approach combining X-ray Photoelectron Spectroscopy (XPS) and Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) including Ar cluster ion sputter depth profiling for three dimensional systems is utilized to prove every reaction step of polymer syntheses and to evidence three-dimensional structures at high lateral resolution. By using different marker molecules as well as specific molecule ion fragments, the combination of these two methods enables to obtain the precise characterization and evaluation of the different polymeric systems.

We present our results on the implementation of new methods for precise surface analysis of polymers. Starting with the investigation of molecular layered systems prepared via electrografting of surfaces followed by successive thiol-yne or thiol-ene reactions, we show controlled functionalization on silicon as well as on highly oriented pyrrolytic graphit substrates. Finally the developed strategy will be transferred to real graphite electrodes. This is an important step to design and tailor the properties of artificial solid electrolyte interfaces (SEI) for lithium ion batteries.

From the characterization of these two dimensional systems (according to the surface analytical tasks), we follow up with polymer systems with three dimensional analysis questions. We present analytical results of network formation using the *Para*-fluoro-thiol reaction and strategies for the confirmation of polymer position after polymerization within defined geometries. Surface analytical recipes to confirm synthesis routes were established. The analytical results of the three dimensional chemical picture are taken to further optimize the synthesis routes and network properties.

We kindly acknowledge the SFB 1176, funded by the German Research Council (DFG), in the context of projects B2, C1, C4 and Z1 for funding. The K-Alpha+ instrument was financially supported by the Federal Ministry of Economics and Technology on the basis of a decision by the German Bundestag.

10:00am **AS+BI+MI-MoM6 Combining Monoatomic- and Cluster Ion Sputtering in ToF-SIMS and XPS Depth Profiling of Organic-inorganic Multilayer Structures**, ***Eric Langer***, *J.-P. Barnes, O.J. Renault, T. Maindron,* CEA-Leti, France, *L. Houssiau,* University of Namur, Belgium

Organic electronics have risen to great importance in the world of consumer electronics. Especially organic light emitting diode (OLED) displays have brought new possibilities to the market. However, organic materials are more susceptible to electrical dysfunctions than conventionally used inorganic materials. This leads to a shortened lifetime for those materials. Environmental impacts like humidity or ultraviolet irradiation can create chemical reactions that lead to dark spots and device failures. Additionally, the flow of current through the device can further promote device degradation and can even induce migration and diffusion of dopants and small molecules. Precise chemical depth profiling is therefore essential to identify sources of failure and improve the device lifetime of organic electronics. Surface analysis techniques such as time-of-flight secondary ion mass spectrometry (ToF-SIMS) and x-ray photoelectron spectroscopy (XPS) are efficient tools to characterize the chemical composition in depth. With the recent introduction of gas cluster ion beam (GCIB) sources, it is possible to sputter through organic materials without inducing a significant amount of damage to the sample [1]. Typically, argon clusters (1000 – 5000 atoms per cluster) with low energy per atom ratios (1 – 5 eV/atom) are used for gentle sputtering. However, these low energies are not sufficient to break the atomic bonds in inorganic materials. This poses a major problem in the characterization of hybrid inorganic-organic devices.

In this work, we present an approach to overcome the difficulties in depth profiling of inorganic-organic interfaces. Green OLED devices are characterized by ToF-SIMS depth profiling using GCIB as well as monoatomic sources for sputtering. This allows for precise tracking of characteristic chemical species in both the inorganic and the organic parts of the multilayer structures. Additionally, XPS depth profiling is used to measure the sputter induced damage during analysis [2]. We show, that by optimizing the sputter parameters, the sputter induced damage can be minimized and precise and reliable chemical information of hybrid inorganic-organic devices can be gained by combining ToF-SIMS and XPS analysis.

This work was carried out on the Platform for Nanocharacterization (PFNC) at the CEA Grenoble.

[1] Ninomiya, S ; Ichiki, K ; Yamada, H ; Nakata, Y ; Seki, T ; Aoki, T ; Matsuo, J Rapid Comm. Mass Spec. **23** 20 (2009) 3264.

[2] Miyayama, T ; Sanada, N ; Bryan, SR ; Hammond, JS ; Suzuki, M ; Surf. Interface Anal. **42** 9 (2010) 1453

10:40am **AS+BI+MI-MoM8 Ultra High Surface Sensitivity – Elemental Analysis of the Outer Layer**, ***Thomas Grehl***, *P. Brüner, H.H. Brongersma,* ION-TOF GmbH, Germany

In materials science and applications, the outer surface plays a vital role for a range of properties and in general for the interaction of a solid with its surroundings. The chemical properties of the surface govern macroscopic properties like wettability/contact angle, but also the chemical interactions as in catalysis, corrosion or thin film growth. The outer surface and its understanding is crucial for catalysis, fuel cells, thin film formation, nanoparticles and a wide range of other processes.

The analysis of the outer surface is frequently hampered by the fact that the origin of the signal is not completely limited to the first atomic layer, but bulk and surface signals are mixed. This issue is avoided in the case of Low Energy Ion Scattering (LEIS). The elemental composition of the outer atomic layer is determined quantitatively and separately from deeper layers. We will demonstrate a number of cases where this is essential to draw the relevant conclusions and reveal surface properties that would not be detected by other surface analytical techniques.

Nevertheless, the combination of complementary techniques is always required to address complex problems. We will demonstrate how the combination of LEIS with other established analytical techniques is beneficial for a comprehensive analysis.

One of these cases is the interaction of Ar cluster ions with a solid sample: it is well known that the sputtering yield of massive argon clusters is some orders of magnitude larger for organic than for inorganic materials. Therefore, Ar cluster beams have been discussed as a means of removing atmospheric adsorbents from surfaces prior to analysis. Using thin film samples, we have evaluated this approach applying LEIS in order to detect the removal of the organic material and the influence on the underlying inorganic surface. Despite the low sputtering yield for the inorganic material, a complete removal of the organic material will lead to a significant modification of the inorganic surface even when the actual erosion is limited.

Other examples from nanoparticles, catalysis and thin films will support the importance of outer layer surface analysis for materials research and other applications.

11:00am **AS+BI+MI-MoM9 Towards Predictive Understanding of Li-S Battery Materials through Multimodal Analysis**, ***Vijayakumar Murugesan***, *K. Han, M.I. Nandasiri, V. Shutthanandan, S. Thevuthasan, K.T. Mueller*, Pacific Northwest National Laboratory

Comprehensive understanding about the interfacial reactions between electrode and electrolyte is the major knowledge gap which inhibit the development of the lithium sulfur (Li-S) batteries. Despite numerous studies, the interfacial reaction mechanism such as SEI layer evolution and polysulfides dissolution process is still unclear. Hence, it is critical to develop a multi-modal approach that can provide unprecedented chemical imaging of complex interfaces in wide lateral (ranging from subatomic to micron) and temporal scales (few ns to seconds). Herein, we report an *in-situ* X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS) and nuclear magnetic resonance (NMR) combined with ab initio molecular dynamics (AIMD) computational modelling to gain fundamental understanding about the complex interfacial interactions in Li-S batteries. A multi-modal approach involving AIMD modelling and in situ XPS and NMR characterization uniquely reveals the chemical identity and distribution of active participants of interfacial reactions as well as the -battery capacity fading mechanism.

11:20am **AS+BI+MI-MoM10 Combined use of Back Side SIMS and FIB Sample Preparation**, ***Mikhail Klimov***, University of Central Florida

When profiling multilayered samples or even a homogeneous samples with rough surface SIMS depth resolution can suffer a rapid deterioration, particularly when polycrystalline metal layers are concerned. The back side SIMS was traditionally used to alleviate a loss of depth resolution during front side depth profiling. The traditional back side SIMS sample preparation involves painstaking polishing or/and ion milling, that requires considerable skills to produce a high quality finish surface that is parallel to front surface and terminated not too far from the interface of interest. Also, because the traditionally prepared sample is relatively large, the precise site specificity is, in general, unattainable.

I offer a relatively expedient FIB sample preparation (~2hrs.) for back side SIMS analysis at precise location and at exact distance from the front surface. The FIB sample extracted from the bulk has a typical lateral dimensions of 10 µ by 10 µ or less. In order to analyze such a small area, even smaller ion beam is required with diameter of 1µ or less to provide good depth resolution and high sensitivity. Also, it’s very much desirable that the ion beam was Oxygen or Cesium to achieve a secondary ion yield enhancement, particularly important for small area analysis. In my case, micron and sub-micron beam of O_2^+ ions was produced by RF Plasma source by Oregon Physics that replaced, for the first time, Duoplasmatron on ADEPT1010 Dynamic SIMS System by Physical Electronics.

The FIB sample preparation procedure is discussed in detail and the first back side SIMS results compared to the front side depth profiles.

11:40am **AS+BI+MI-MoM11 Phase Quantification of Mixed TiO_2 Powders by X-ray Photoemission Valence Band Analysis and Raman Spectroscopy**, ***Paul Mack***, *T.S. Nunney,* Thermo Fisher Scientific, UK, *R.G. Palgrave*, University College London, United Kingdom of Great Britain and Northern Ireland

Titanium dioxide is one of the most studied materials in surface science. It has applications in heterogeneous catalysis, dye-sensitised solar cells, bone implants and self-cleaning windows. Many polymorphs of TiO_2 are known to exist but only two occur naturally in abundance: rutile and anatase. Rutile is the more thermodynamically stable form but anatase is more energetically favourable when forming nanoparticles at atmospheric temperature and pressure. The anatase polymorph has been recognised as more photoactive than rutile, although recent research indicates that the greatest photovoltaic efficiencies are achieved in devices that contain a mixture of anatase and rutile. The degree of mixing between two polymorphs influences other material properties, such as catalytic activity. This raises the question: how can one determine the polymorph ratio in a sample that contains a mixture of anatase and rutile?

Quantitative phase analysis of anatase-rutile mixtures by two experimental methods is presented in this work. Spectra of pure reference anatase and rutile were acquired X-ray Photoelectron Spectroscopy (XPS) and Raman spectroscopy. These spectral shapes were then used to fit similar data from mixed phase samples. XPS and Raman spectroscopy give information from different depth regions in a sample. The surface sensitive character of XPS yields a surface phase fraction of anatase and rutile. Mixed phase samples were prepared from high and low surface area anatase and rutile powders. In this work, the surface phase fraction of anatase was found to be linearly correlated with photocatalytic activity of the mixed phase samples, even for samples with very different anatase and rutile surface areas.

Spectroscopic Ellipsometry Focus Topic
Room: 9 - Session EL+AS+EM+TF-MoM

Application of SE for the Characterization of Thin Films and Nanostructures
Moderator: Tino Hofmann, University of North Carolina at Charlotte

8:20am **EL+AS+EM+TF-MoM1 Ultra-thin Plasmonic Metal Nitrides: Optical Properties and Applications**, ***Alexandra Boltasseva***, Purdue University **INVITED**

Transition metal nitrides (e.g. TiN, ZrN) have emerged as promising plasmonic materials due to their refractory properties and good metallic properties in the visible and near infrared regions. Due to their high melting point, they may be suitable for high temperature nanophotonic applications. We have performed comprehensive studies of the temperature induced deviations to the dielectric function in TiN thin films. The studies were conducted on 30 nm, 50 nm, and 200 nm TiN films on sapphire substrates at temperatures up to 900 0C in the wavelength range 350-2000 nm using a custom built in-situ high temperature ellipsometry setup. The results were fitted with a Drude-Lorentz model consisting of one Drude oscillator and 2 Lorentz oscillators. As the temperature is elevated, the real and imaginary parts both begin to degrade. However, the deviations to the optical properties of TiN are significantly smaller compared to its noble metal counterparts, with no structural degradation in the TiN films. In addition to high temperature applications, TiN could also be a potential material platform for investigating light-matter interactions at the nanoscale, since high quality, continuous films of TiN can be grown on substrates such as MgO and c-sapphire down to just a few monolayers. Ultrathin TiN films with thicknesses of 2, 4, 6, 8, and 10 nm were grown on MgOusing DC reactive magnetron sputtering, resulting in high quality films with low roughness. The changes in the linear optical properties were investigated using variable angle spectroscopic ellipsometry at angles of 50° and 70° for wavelengths from 400 nm to 2000 nm. A Drude-Lorentz model consisting of one Drude oscillator and one Lorentz oscillator was used to fit the measurements. As the thickness decreased, an increase in the losses and a decrease in the plasma frequency was observed. However, the films remained highly metallic even at 2nm, demonstrating that they could be used for nanophotonicapplications, including nonlinear optical devices and actively tunable plasmonic devices.

9:00am **EL+AS+EM+TF-MoM3 Magnetron Sputtering of TiN Coatings: Optical Monitoring of the Growth Process by Means of Spectroscopic Ellipsometry**, ***Jiri Bulir***, *J. More Chevalier, L. Fekete, J. Remiasova, M. Vondracek, M. Novotny, J. Lancok*, Institute of Physics ASCR, Czech Republic

The plasmonic applications requires search for novel materials with metal-like optical properties and low optical losses. Transition metal nitrides such as TiN, TaN, ZrN, HfN, NbN exhibit metallic properties depending on concentration of free-carrier of charge. Their plasmonic properties can be tuned by deposition parameters controlling the film structure and the stechiometry.

In this work, we deal with study of growth process of TiN films. The films are grown by RF magnetron sputtering on fused silica, silicon and MgO substrates at substrate temperature ranging from 20°C to 600°C. The growth process is monitored using in-situ spectral ellipsometer in spectral range from 245 to 1690 nm. The ellipsometric data, which are obtained during the deposition process, are attentively analysed using mathematical models based on Drude-Lorentz oscillators.

The Lorentz oscillators are used for description of interband transition in ultraviolet and visible spectral range, whereas the Drude oscillator describes the free-electron behavior in the infrared spectral range. We show that the free-electron behavior is affected by thickness of the ultrathin coatings due to electron scattering effects at the interfaces. Number of physical parameters such as free-electron concentration, Drude relaxation time and electrical conductivity is estimated at each stage of the deposition process by analysis of dielectric functions using the mentioned model. The resulting evolution of the electrotransport properties during the TiN film growth is presented. Special attention is devoted to the initial nucleation stage when the free-electron behaviour is significantly influenced by the interface between the substrate and the TiN film. Based on evolution of electrotransport properties, we discuss differences between polycrystalline growth of TiN film on Si and fused silica substrates and epitaxial growth on MgO substrates.

The accomplished TiN coatings are analyzed using infrared ellipsometer operating in spectral range from 1.7μm to 30μm where the optical constants are infuenced most importantly by free-electron behaviour. The obtained results are compared with those obtained by the in-situ ellipsometer. Special attention is focused on scattering of free electrons at grain boundaries and at the TiN layer interfaces. The estimated parameters are correlated with structure changes such as grain coarsening and surface morphology. The crystallinity is analysed by X-ray Difractometry. The surface morphology of the completed coatings is studied using Atomic Force Microscopy and Scanning Electron Microscopy. The TiN film stechiometry is estimated by X-ray Photoemission Spectroscopy.

9:20am **EL+AS+EM+TF-MoM4 Variable Temperatures Spectroscopic Ellipsometry Study of the Optical Properties of InAlN/GaN Grown on Sapphire**, *Y. Liang*, Guangxi University, China, *H.G. Gu*, Huazhong University of Science and Technology, China, *J. Xue*, Xidian University, China, ***Chuanwei Zhang***, Huazhong University of Science and Technology, China, *Q. Li*, Guangxi University, China, *Y. Hao*, Xidian University, China, *S.Y. Liu*, Huazhong University of Science and Technology, China, *Q. Yang, L. Wan, Z.C. Feng*, Guangxi University, China

Indium aluminum nitride (InAlN), a prospective material for lattice matched confinement layer, possesses the potential to improve the reliability and performance of high electron mobility transistors (HEMTs).[1] One of the important advantages of InAlN alloy is the possibility of growing in-plane lattice-matched to GaN for an indium content of around 17%. However, the bandgap we expected is hindered by the growth of high-quality InAlN films due to the phase separation and nonuniform composition distribution.[1-2]

In this work, InAlN/GaN heterostructures, grown by pulsed metal organic chemical vapor deposition (PMOCVD) on c-plane sapphire substrates, were investigated by a dual rotating-compensator Mueller matrix ellipsometer (ME-L ellipsometer, Wuhan Eoptics Technology Co. Ltd., China). The experimental data (Ψ and Δ), covering the wavelength (λ) range from 193 nm up to 1700 nm at 1 nm step or energy (E) from 0.73 eV to 6.43 eV, were obtained by variable temperatures spectroscopic ellipsometric (VTSE) in three angles (50°, 55° and 60°). The Eoptics software was utilized to fit VTSE data using Tauc-Lorentz multiple oscillator modes. By analyzing the fitting results, the optical constants of the InAlN at variable temperatures (25℃-600℃) were obtained. The peak value of the refractive index increases from 269 nm to 284 nm with increasing temperature. The bandgaps are 4.57 eV and 4.35 eV at the temperature 25℃and 600℃, respectively. These results demonstrated that InAlN/GaN has a high thermal stability, scilicet no significant performance degradation in high temperature environment.

Reference

[1] Wenyuan Jiao, Wei Kong, Jincheng Li et al, Characterization of MBE-grown InAlN/GaN heterostructures valence band offsets with varying In composition, AIP ADVANCES 6, 035211 (2016).

[2] JunShuai Xue, JinCheng Zhang, Yue Hao, Investigation of TMIn pulse duration effect on the properties of InAlN/GaN heterostructures grown on sapphire by pulsed metal organic chemical vapor deposition, Journal of Crystal Growth 401, 661 (2014).

9:40am **EL+AS+EM+TF-MoM5 Optical Properties of $Cs_2AgIn_{(1-x)}Bi_xCl_6$ Double Perovskite Studied by Spectroscopic Ellipsometry**, ***Honggang Gu***, *S.R. Li, B.K. Song, J. Tang, S.Y. Liu*, Huazhong University of Science and Technology, China

During the past several years, the organic-inorganic lead halide perovskites ($APbX_3$, A = CH_3NH_3 or NH_2CHNH_2, X = Cl, Br, or I) have been promising materials for photovoltaic, photoelectric -detecting and light-emitting devices due to their outstanding photoelectric properties, such as broad absorption range, high quantum efficiency, ultrafast charge generation, high charge carrier mobility and long charge carrier lifetime and diffusion length. However, there are two remaining challenges that need to be addressed in order to apply these materials to photoelectric productions, namely the compound stability and the presence of lead. Most recently, lead-free metal halide double perovskites, such as $Cs_2AgBiCl_6$ and $Cs_2AgInCl_6$, have attracted extensive attention because of their nontoxicity and relative air-stability. In the study and application of these perovskite materials, the knowledge of their optical properties, such as the bandgap and the basic optical constants, is of great importance to predict the photoelectric characteristics and dig the potential of the materials.

Spectroscopic ellipsometry (SE) has been developed as a powerful tool to characterize the optical properties as well as structure parameters of novel materials, thin films and nanostructures. In this work, we study the optical properties of $Cs_2AgIn_{(1-x)}Bi_xCl_6$ perovskites by a spectroscopic ellipsometer (ME-L ellipsometer, Wuhan Eoptics Technology Co., Wuhan, China). The refractive index and the extinction coefficient of $Cs_2AgIn_{(1-x)}Bi_xCl_6$ with different composition coefficient x of bismuth are determined by the ellipsometer over the wavelength range of 250-1000nm. We find that the presence of bismuth introduces two critical points in the optical constant spectra of the perovskites, i.e., 315nm and 382nm in the refractive index spectra and 300nm and 375nm in the extinction coefficient spectra, respectively. Moreover, there is a red shift in the bandgaps and significant increase in both the refractive index and the extinction coefficient with the increase of composition coefficient x of bismuth.

10:00am **EL+AS+EM+TF-MoM6 Charge Carrier Dynamics of Aluminum-doped Zinc Oxide Deposited by Spatial Atomic Layer Deposition**, ***Daniel Fullager***, *G. Boreman, T. Hofmann,* University of North Carolina at Charlotte, *C.R. Ellinger*, Eastman Kodak Company

Transparent conductors for displays, backplanes, touchscreens and other electronic devices are an area of active research and development; in this manner, aluminum-doped zinc oxide (AZO) has shown promise as an ITO replacement for some applications. Although there have been numerous reports on the optical properties and electrical conductivity of AZO, there has not yet been a Kramers-Kronig consistent dispersion model fully describing the charge carrier dynamics. In this presentation, we will report on the model dielectric function of AZO from the combination of UV-Vis and IR spectroscopic ellipsometry. A model dielectric function that describes the optical response over this wide spectral range will be presented and discussed. In particular, we will present a comparison between the commonly used extended Drude models and the dielectric function developed here in light of results obtained from density functional theory calculations.

The AZO films analyzed in this study were deposited using a spatial atomic layer deposition (SALD) process. While AZO can be deposited by several techniques, including sputtering, chemical vapor deposition (CVD), and atomic layer deposition (ALD), ALD does allow for the greatest ability to control the aluminum-doping level of AZO. However, the range of substrate sizes and form factors addressable by traditional chamber ALD are limited. Conversely, spatial ALD (SALD) is an atmospheric pressure, roll-compatible ALD process that enables the materials property control of ALD to be translated into a wider range of applications spaces. Furthermore, the use of selective area deposition in a "patterned-by-printing" approach enables the high-quality AZO deposited by SALD to be easily patterned, offering an integrated and facile path for manufacturing optical and electronic devices.

10:40am **EL+AS+EM+TF-MoM8 Broad Range Ellipsometry Shining Light onto Multiphase Plasmonic Nanoparticles Synthesis, Properties and Functionality**, ***Maria Losurdo***, CNR-NANOTEC, Italy **INVITED**

How rich are the physics, interface chemistry and optical properties associated with the surface plasmons of metal nanostructures and their potential for manipulating light at the nanoscale! For many technological applications nanoparticles (NPs) are supported on a substrate, and at the nanoscale, interaction and interfaces with the support become very important. We have demonstrated that the substrate/NPs interaction is the key to engineering not only the shape but also the crystalline phase of NPs.

This contribution will present and explore fundamental and applied aspects of multiphase core-shell plasmonic NPs supported on substrates of technological interest using various diagnostic tools, which comprise: (i) spectroscopic ellipsometry spanning the THz, IR, visible, and UV wavelength ranges, (ii) variable angle Muller Matrix ellipsometry to qualify size effects on anisotropy and depolarization of samples, (iii) *in-situreal-time* spectroscopic ellipsometry to understand growth and tailor particle size which ultimately controls the plasmon resonance, and (iv) various imaging and microscopies techniques to elucidate the interplay between the nanostructure of multiphase nanoparticle and their functionality.

The case studies involve liquid-shell/solid-core plasmonic NPs (Ga, Ga/Mg), plasmon-catalytic core/shell Ga/Pd and plasmon-magnetic Ni/Ga NPs supported on various substrates (glass, plastics, sapphire) that control their crystalline phases.

We will start with a description of the *real-time* ellipsometry capabilities in monitoring the growth of those multiphase core/shell NPs to detect the formation of the various phases in situ and to control the resulting plasmon resonance.

The discussion then will shifts to a description of fundamental of thermodynamics of substrate supported multiphase NPs and how their growth dynamics is controlled by the interface energies, and how those new phenomena can be highlighted by real-time ellipsometry.

Ex-situ corroborating measurements of Mueller-matrix ellipsometry and hyperspectral cathodoluminescence spectroscopy and imaging will be presented to discuss phenomena of depolarization and of interaction of NPs resulting from the self-assembly.

Finally, since those NPs enable active plasmonics, we demonstrate the implications of the multi-phase nature of NPs, as well as solid-liquid phase coexistence on the plasmon resonance (LSPR) of supported NPs and on its exploitation to follow in real time phenomena in their application in catalysis (hydrogen storage and sensing) and optomagnetism and possible future directions.

The contribution of the H2020 European programme under the project TWINFUSYON (GA692034) is acknowledged

11:20am **EL+AS+EM+TF-MoM10 Use of Evolutionary Algorithms for Ellipsometry Model Development and Validation using Eureqa**, ***Neil Murphy***, Air Force Research Laboratory, *L. Sun*, General Dynamics Information Technology, *J.G. Jones*, Air Force Research Laboratory, *J.T. Grant*, Azimuth Corporation

Eureqa, developed by Nutonian Inc., is a proprietary modeling engine based on automated evolutionary algorithms. In this study, we utilized Eureqa to parameterize both the amplitude and phase difference data for reactively sputtered thin films. Specifically, evolutionary algorithms are used to develop and validate models for fitting raw ellipsometric data for a variety of optical materials including SiO_2, Ta_2O_5, and Aluminum Zinc Oxide. These films, deposited using pulsed DC magnetron sputtering, were deposited on both silicon and fused quartz substrates, and measured using a J.A. Woollam VASE system. The resulting models are then compared to traditional models that are currently utilized to fit the candidate materials systems.

11:40am **EL+AS+EM+TF-MoM11 Excitonic Effects on the Optical Properties of Thin ZnO Films on Different Substrates**, ***Nuwanjula Samarasingha***, *Z. Yoder, S. Zollner*, New Mexico State University, *D. Pal, A. Mathur, A. Singh, R. Singh, S. Chattopadhyay*, Indian Institute of Technology Indore, India

The presence of excitonic features in the optical constants of bulk semiconductors and insulators has been known for many years. In Si, Ge, and GaAs, the E_1 critical points are strongly enhanced by two-dimensional excitons. Three-dimensional excitons have been seen in ellipsometry spectra for GaP and Ge. In addition to these semiconductors, wide band gap materials like ZnO exhibit strong excitonic features in the dielectric function (ε) which is directly related to the electronic band structure. The top valence band at the Γ point in the Brillouin zone is split into three bands by spin orbit and crystal field splitting. The corresponding free exciton transitions between the lowest conduction band and these three valence bands are denoted by A, C (Γ_7 symmetry) and B (Γ_9 symmetry). The transition from the B subband is forbidden for light polarized parallel to the optical axis (extraordinary dielectric function). ZnO is attractive for optoelectronic device applications due to its large excitonic binding energy of 60 meV at room temperature.The influence of this excitonic absorption on ε was described by Tanguy [1].

Here we investigate the behavior of excitons in c-oriented ZnO thin films grown on Si (smaller band gap than ZnO) and SiO_2 (larger band gap than ZnO) substrates using variable angle spectroscopic ellipsometry and FTIR ellipsometry. We also performed X-ray diffraction (XRD), X-ray reflectivity (XRR), and atomic force microscopy (AFM) to characterize the structural properties of our ZnO films.

In a thin epitaxial layer on a substrate with a different band gap, the wave functions of the electron and hole are strongly modified. In ZnO (band gap 3.37 eV) grown on a large-gap SiO_2 substrate (type-I quantum well), both the electron and the hole are confined, which leads to an increase in the dipole overlap matrix element. Therefore, the real and imaginary part of ε of thin ZnO layers on SiO_2 are much larger than in the bulk and increase monotonically with decreasing thickness.

On the other hand, in a staggered type-II quantum well (ZnO on Si), either the electron is confined, or the hole, but not both. Therefore, the overlap dipole matrix element is strongly reduced. Therefore, ε of thin ZnO layers on Si is much smaller than in the bulk and decreases monotonically with decreasing thickness. We will fit our ellipsometric spectra by describing the dielectric function of ZnO using the Tanguy model [1]. We will analyze the dependence of the excitonic Tanguy parameters on quantum well thickness and substrate material.

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Plasma Science and Technology Division
Room: 21 - Session PS+AS+SE-MoM

Atmospheric Pressure Plasmas

Moderators: Olivier Guaitella, Ecole Polytechnique - CNRS, France, Seiji Samukawa, Tohoku Univeversity, AIST, Japan

8:20am **PS+AS+SE-MoM1 Study of Atmospheric-pressure kHz Multi-jet Plasma System**, ***Vladimir Milosavljevic***, *J. Lalor, L. Scally, P.J. Cullen*, Dublin Institute of Technology, Ireland

Non thermal plasmas can be generated in laboratory conditions using generic, readily available and easily sourced components. Examples include glass tubing, copper or stainless wire electrodes, metal mesh, plastic enclosures, and step-up transformer based power supplies. Such sources, although effective, may not offer optimised conditions or efficiencies. In many cases they may not sustain extended operation due to excess thermal and electrical breakdown. Second-generation laboratory apparatus and scaled up designs involve selected materials, custom machined components, electrodes based on calculated requirements, and suitably designed or sourced power supplies. These assemblies will offer a more accurate theoretical and empirical view of the plasma performance. The inclusion of a material selection software tool for the rational selection of engineering materials can provide detailed information relating to the mechanical thermal and electric properties. Developing a non-thermal atmospheric plasma source involves three important factors for material selection. Firstly the application and operating conditions of the design needs to be examined; is it to be handheld, exposed to ambient air or contained in an enclosure. For many plasma sources, certain polymers offer an ideal material, for other configurations, composites or metals may be best. Secondly, does the source need to facilitate a controllable environment in which to generate the plasma, in other words, is it necessary to purge or evacuate the enclosure in order to accurately control the gas chemistry, if this is the case, a choice of material for this housing and containment area must be considered. The third factor is the material selection for the conducting elements, namely the cables, electrodes and grounding components. Typical electrode metals include copper, aluminium, brass and stainless steel.

In this work 12 circular plasma jets are presented. They are designed and built in-house, and power up with a single phase generator of 10-30 kV, at 10-100 kHz that powers up to 2 kW. Voltage-current measurements and optical emission spectroscopy (OES) are applied for optimization of transient discharges operated for several different gas chemistry at atmospheric pressure. The influence of applied voltage, frequency, gas flow rate and gas chemistry in relation with the OES signal, plasma plume formulation, gas velocity and electrical properties of plasma jets are the objectives of this study.

This work was funded under the ’PlasmaGrain’ project funded by the SFI, Republic of Ireland.

8:40am **PS+AS+SE-MoM2 Synthesis of Nitrates by Atmospheric Microplasma Over Water : Effect of the Experimental Parameters and Intermediate Species**

Nicolas Maira, *C. De Vos*, *F. Reniers*, Université Libre de Bruxelles, Belgium

Nowadays, nitrates are used mainly as fertilizers in agriculture. They are produced by the combination of the Haber-Bosch and Ostwald process. Industry, throughout the years, has increasingly optimized the energetic yield of this synthesis. Nevertheless, this method requires the use of a hydrogen source, essentially extracted from fossil fuel. Moreover, nitrates synthesized in colossal plant factories have to be shipped to the end-user. However, in some applications such as hydroponics or urban agriculture, the local production of pure nitrates fertilizers directly available in the flowing water feeding system would be of great interest.

In this study, the same philosophy as for the ozone process is applied: taking advantage of the composition of natural air in order to synthesize nitrates directly in a solution [1]. The mechanism of formation of nitrates using an atmospheric microplasma discharge operating in air or in argon in an open air environment is investigated. The effect of the treatment time, the discharge current and power, the water surface – capillary distance, and the solution pH on the formation of nitrogen oxides in the gas phase and in solution is studied. The liquid phase is analyzed by Ionic Chromatography (IC), UV-visible spectrometry (UV-vis) and pH-metry, whereas the gas phase is probed by Optical Emission Spectroscopy (OES) and atmospheric Mass Spectrometry (MS).

The total amount of NO_x formed in a solution shows a linear trend with the total charge injected into the plasma with however different slopes for nitrites (NO_2^-) and nitrates (NO_3^-). The reaction mechanism involves the formation of gas phase NO, as evidenced by OES. It is known that the synthesis of nitrates is pH-dependent [2]. In an acidic solution with a pH below 3, the formation of nitrates is favored whereas a higher pH allows the formation of nitrites which are oxidized in nitrates after the treatment. The transformation of nitrites into nitrates after plasma synthesis is monitored by IC during time and seems to follow a logarithmic trend. The performed experiments allow the determination of the amount of energy required to form a mole of nitrate in this set-up.

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9:00am **PS+AS+SE-MoM3 Plasma Catalysis for CO_2 and CH_4 Conversion at Atmospheric Pressure**

A. Ozkan, *S. Chorfi*, *L. Brune*, *T. Visart de Bocarmé*, ***François Reniers***, Université Libre de Bruxelles, Belgium

The field of plasma-catalysis, i.e. combining a plasma process and a catalyst, either inside the plasma or in its post-discharge is gaining importance for the conversion of CO_2 and CH_4 mixtures. Indeed, the combination of plasma and catalysis could not only increase the conversion of these gases, but also orient the reaction(s) towards the synthesis of valuable molecules.

This paper will present first the main factors that influence the conversion and the energy efficiency for the reduction of CO_2 using an atmospheric pressure dielectric barrier discharge. Second, an alumina supported catalyst will be added between the electrodes and its effects on the conversion of pure CO_2, pure CH_4 and CO_2/CH_4 mixtures will be presented. Ni, Co, Cu have been tested, as well as various loadings of Ni.

The conversion is studied by atmospheric mass spectrometry, and the chemical identification of the end products was obtained either by mass spectrometry or gas chromatography.

It is shown that the frequency, the pulse mode, the dielectric nature and thickness strongly influence the conversion and energy efficiency of the reaction, whereas the residence time and the power injected into the discharge modify the conversion[1]. An increase in the Ni loadings leads to an increase in conversion of both CO_2 and CH_4. If CO and H_2, starting molecules for more complex organic chemistry, are always the main products of reaction, C2, C3 and C4 molecules, oxygenated or not are also detected. The effect of the nature of the catalyst on the relative amounts of these molecules is discussed.

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9:20am **PS+AS+SE-MoM4 Aluminium Surface Plasma Treatment at Atmosphere Pressure**

Lucia Bonova, *I.A. Shchelkanov*, *C. Ahn*, *S. Chaudhuri*, *D.N. Ruzic*, University of Illinois at Urbana-Champaign

Plasma surface treatment at atmosphere pressure is a fast growing industry. Among other applications, surface treatment of metals for adhesion and corrosion resistance improvement has attracted widespread interest. Being operated at atmosphere pressure, various types of plasma discharge devices provide efficient, cheap and large scale processing capabilities. In this area, surface treatment of aluminium for surface properties modification is of great interest as it can decrease steps in process for final coating deposition, reduce usage of harmful chemical reagents, which in their turn require costly dispose procedures, and increase functional coatings performance.

The ECAP experiment (Evaporative Coatings at Atmosphere Pressure) was developed at CPMI (Center for Plasma Materials Interaction at UIUC) as a device and a method for multicomponent metal coatings deposition at atmosphere pressure utilizing a 2.45 GHz microwave plasma torch. The device is capable of coating deposition from a solid metal state and from gas carried precursors as well as composites with processing gas like ZrO. These capabilities make ECAP a very flexible tool for gradient coating deposition for surface functionalization and adhesion improvement. In this gradient coating, the alumina facing materials is gradually replaced with a second layer material with perfect adhesion for final functional coating.

Current work discusses several methods, which were used to improve aluminium surface wettability and adhesion to an epoxy. As a fundamental experiment, we have conducted the simple treatment on aluminium plate by ECAP which operated with feedstock gas of evaporated H_2O and He. It shows remarkable enhanced epoxy adhesion on aluminium sample against the control condition. System configuration for roll-to-roll applications and broad area coatings/cleaning are also discussed.

9:40am **PS+AS+SE-MoM5 The Role of Bulk Liquid Transport Processes in the Plasma-Liquid Interfacial Chemistry**

Selma Mededovic Thagard, *M. Vasilev*, *D. Bohl*, *P. Conlon*, Clarkson University **INVITED**

Plasmas formed directly in and contacting a liquid are powerful sources of reactive radicals, ions and high-energy electrons and have been successfully used to sterilize water and fruit juices, purify water, synthesize materials and nanoparticles, and for applications in plasma medicine, electrical transmission, and polymer surface treatment. Nevertheless, despite the obvious versatility in processing capabilities, the optimization and broader application of electrical discharge plasmas in and contacting a liquid have been limited due to a general lack of understanding of the underlying physical and chemical processes occurring at the plasma-liquid interface. Despite the significant progress that has been made towards understanding interfacial chemistry of plasmas in the last decade or so (especially for air plasmas contacting water), relative contributions of plasma processes such as formation and diffusion of reactive species and bulk liquid processes such as electrohydrodynamic flow to interfacial dynamics have not been yet determined.

This work investigates the extent to which bulk liquid processes, primarily bulk liquid composition and plasma-induced electrohydrodynamic flow control the rates of chemical reactions at a plasma-liquid interface. We have determined the efficacy of the plasma process for treatment of a wide range of different compounds and used the results of this investigation to construct a model to predict the approximate treatability of any compound based on just a few of the compound's physical properties. Experiments with different initial bulk liquid concentrations of non-surfactant and surfactant compounds have also been performed to investigate how interfacial compound concentration affects its removal rate. Particle Image Velocimetry has been used to quantify the surface velocity of a liquid as a function of its chemical composition.

10:40am **PS+AS+SE-MoM8 Efficiency of Electrolytic Reduction of Aqueous Metal Salts to Metal Nanoparticles at a Plasma-Liquid Interface**, *S. Ghosh*, ***Ryan Hawtof***, Case Western Reserve University, *P. Rumbach, D.B. Go*, University of Notre Dame, *R. Akolkar, R.M. Sankaran*, Case Western Reserve University

Electrolytic cells with a plasma serving as one or both of the electrodes eliminate the solid metal and allow electrochemical reactions to be carried out at a gas-liquid interface. This is particularly beneficial for the synthesis of metal nanoparticles from metal salts since the deposition of a thin film onto the electrode is avoided. However, because of the complexity of the plasma and the resulting interfacial reactions, the mechanism for metal nanoparticle formation remains unknown.

Here, we designed experiments to understand the mechanism of the reduction of silver nitrate ($AgNO_3$) to silver (Ag) nanoparticles by a previously reported atmospheric-pressure, direct current microplasma operated as the cathode. We applied a well-known methodology in electrodeposition to assess the faradaic efficiency whereby the mass of the synthesized material is compared with the theoretical amount of mass estimated from the charge injected into solution. A faradaic efficiency of 100% would indicate that all the charge is going towards the desired reduction of Ag cations to solid Ag, $Ag^+ + e^-$ --> Ag^0, whereas an efficiency less than 100% would suggest that there are side reactions, most probable of which is the second order recombination of (solvated) electrons to form hydrogen gas and hydroxide ions, $e^-_{(aq)} + e^-_{(aq)} + 2H_2O_{(l)}$ --> $H_{2(g)} + 2OH^-_{(aq)}$.

We find that at a relatively high $AgNO_3$ concentration in the bath, the faradaic efficiency depends weakly on the current, reaching values of 100% at 2 mA and decreasing to slightly less than 100% at 6 mA. To corroborate these measurements, the mass change of a Ag foil anode which oxidizes in solution by the reverse of the cathode reaction, Ag^0 --> $Ag^+ + e^-$, was compared and found to yield slightly lower efficiencies, but with the same overall trend. At constant current and varying $AgNO_3$ concentration in the bath, the faradaic efficiency was found to drastically decrease to less than 100%. We interpret these results as follows. The kinetics of the primary reactions, Ag^+ reduction and second order recombination, depend on the respective rate constants which are similar (3.7×10^{10} M/s and 5.5×10^9 M/s) and the reactant concentrations. At low current or high $AgNO_3$ concentration, the rate of Ag^+ reduction is higher than second order recombination and the faradaic efficiency approaches 100%. Conversely, the rate of second order recombination is higher than Ag^+ reduction at high current or low $AgNO_3$ concentration, lowering the faradaic efficiency. A reaction model was developed to support these interpretations.

11:20am **PS+AS+SE-MoM10 Amorphous Indium Zinc Oxide (IZO) Semiconductor Films Grown by Atmospheric Plasma-Enhanced Spatial ALD for Application as High-Mobility Channel in Thin Film Transistors**, *A. Illiberi, I. Katsouras, S. Gazibegović, B. Cobb, E. Nekovic*, TNO-Holst Centre, Netherlands, *W. van Boekel, C. Frijters*, TNO-Solliance, Netherlands, *J. Maas*, TNO-Holst Centre, Netherlands, ***Fred Roozeboom***, TNO-Holst Centre & Eindhoven University of Technology, Netherlands, *Y.L.M. Creyghton*, TNO-Solliance, Netherlands, *P. Poodt*, TNO-Holst Centre, Netherlands, *G. Gelinck*, TNO-Holst Centre & Eindhoven University of Technology, Netherlands **INVITED**

Less than a decade ago, InGaZnO has been reported as a new Amorphous Oxide Semiconductor (AOS) channel material replacing conventional amorphous silicon (a-Si:H) for application in thin-film transistor (TFT) circuits in display back panels [1]. Among these, indium zinc oxide (IZO) is emerging as the most promising AOS candidate for next-generation displays based on oxide TFTs because it combines a very high electron mobility with excellent optical transmission and thermal stability [2,3].

We have grown InZnO thin films by plasma-enhanced spatial atomic layer deposition (s-ALD) [4,5] and these layers have been manufactured into oxide TFT and ring oscillator devices which outperform the state-of-the-art. We will describe the growth of InZnO at atmospheric pressure and high deposition rates (~ nm/sec) starting with a short explanation of the basics and the advantages of this novel deposition technique including the use of a special atmospheric plasma source design of the so-called Surface Dielectric Barrier Discharge (SDBD) type [6]. Next, we will show that by varying the ratio of the trimethyl indium and diethyl zinc chemical precursor vapors, the In/(In+Zn) ratio of the film can be accurately tuned over the entire composition range from zinc oxide to indium oxide. TFT test devices with an In/Zn ratio of 2:1 show very high field-effect mobility exceeding 30 $cm^2/V.s$ (Fig. 1), excellent thermal (Fig. 2) and bias stress stability. We will further demonstrate the scalability of the IZO TFTs by fabricating 19-stage ring oscillators operating at 200 kHz which outperform the state-of-the-art.

This superior electrical performance, in combination with the intrinsic advantages of spatial ALD demonstrate the great potential of this atmospheric plasma concept for application in commercial manufacturing of low-cost and large-area AOS-based electronics.

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Plasma Science and Technology Division
Room: 23 - Session PS+AS-MoM

Plasma Processing of Challenging Materials

Moderators: Erik V. Johnson, LPICM, Ecole Polytechnique, France, Osamu Sakai, The University of Shiga Prefecture

8:20am **PS+AS-MoM1 Control of Plasma Doping Conformality in FinFET Arrays**, ***Mona Ebrish***, *O. Gluschenkov*, IBM Research Division, *M.J.P. Hopstaken*, IBM T.J. Watson Research Center, *F. Torregrosa*, Ion Beam Services

FinFET devices are rapidly emerging as a standard transistor architecture for extending CMOS scaling beyond the 22 nm technology node because of superior electrostatic channel control. One practical challenge is to achieve a high degree of conformality for source/drain (S/D) extension doping along the Fin sidewalls. Conformal extension doping is crucial to minimize finFET series resistance while maintaining electrostatic channel control. Precise control of transistor characteristics over large-scale CMOS circuits and systems mandates that the extension doping and its conformality be maintained over arrays of finFETs with tight fin pitch. Plasma doping, with its wide distribution of impinging ion angles, provides an alternative to conventional ion beam implantation for fin array sidewalls. The traditional 1D Secondary Ion Mass Spectrometry (SIMS) depth profiling technique is unable to quantify the doping profiles in fin array sidewalls and hence the 1.5D SIMS approach (SIMS through array of fins) is used in this study. The retained sidewall dose measured by 1.5D SIMS is compared to a predicted number of impinging plasma ions that arrive to the fin array with certain angle and energy distributions dependent on the plasma conditions. This comparison takes into account the impinging ion cut off angle caused by adjacent fin shadowing in tight-pitch arrays. Based on those findings, a tuning of the plasma conditions was applied to obtain better than 50% dopant uniformity along the Fin sidewalls. The ability to control impinging ion angle distributions in plasma doping provides a valuable tool for improving doping conformality in tight-pitch fin arrays.

8:40am **PS+AS-MoM2 Study of Plasma-etching Parameter Impacts on Two-dimensional Electron Gas Degradation in AlGaN/GaN Heterostructures**, ***Frédéric Le Roux***, *P. Burtin, N. Posséme, A. Torres, S. Barnola*, CEA-Leti, France

Formation of the two-dimensional electron gas (2DEG) in AlGaN/GaN heterostructrures is the key-point for successful development of GaN-based power-electronics such as High Electron Mobility Transistors and diodes.

Today, plasma-etching are considered as one of the most critical step in fabrication of such devices. Indeed plasma etching can lead to charge generation (depleting the channel)[1,2], AlGaN amorphisation (modifying the structure and the polarisations of the AlGaN)[3,4] or element implantation inducing charges or traps[5].

In this study, we propose to evaluate the impact of several plasma parameters (chemical, physical and physico-chemical) on 2DEG degradation occurring during silicon nitride etching (selectively to AlGaN). Experiments have been carried out on 200mm wafers using the following stack: 10nm Si_3N_4/24nm $Al_{0,22}Ga_{0,78}N$/AlN spacer/2µm GaN/buffer layers. The AlGaN degradation has been determine thanks to Rsheet and Hall measurements.

First the impact of a conventional fluorocarbon etch chemistry ($CF_4/CH_2F_2/O_2$/He) on 2DEG degradation will be presented as an ion-energy function. It will be demonstrated that Rsheet is degraded with the ion energy increase and confirmed by the evolution of career- density and mobility.

Then the pure-chemical etching effects (using wet and downstream-plasma etching process) as well as physical etching effects, with ion bombardment, (using Ion Beam Etching process (IBE)) will be discussed in term of Rsheet.

Finally, the benefit of new silicon nitride etching process, which has already been tested and validated for silicon nitride spacer application[6], has been evaluated for diode contact application. This process is based on two steps. In a first step, the film is modified in volume by a He plasma performed in a conventional etch tool (ICP) followed by a second step of selective removal (HF dip) of the modified layer (Si_3N_4) with respect to the non-modified material (AlGaN).

Thanks to this study, the plasma-etching's role in the channel characteristics degradation have been highlighted and linked to the plasma parameter through the Rsheet and Hall measurement evolutions. In order to increase the degradation mechanism understanding engendered by etching steps, physico-chemical characterisations will be developed to determine the degradation sources.

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9:00am **PS+AS-MoM3 Spatiotemporal Non-uniformity of CVD Plasmas and Film Qualities**, ***Masaharu Shiratani***, Kyushu University, Japan **INVITED**

Here we discuss great impact of nanoparticles formed in CVD plasma on uniformity of the plasma and film qualities [1-5]. Uniformity of thickness, composition, structure, and properties is a major concern of plasma CVD films. Multiple precursors including radicals, ions, and nanoparticles contribute to the film formation and hence their flux and flux ratio to the surface determine the film uniformity. Although most studies and text books describe film formation due to radicals and ions, such precursors are predominant only for very low pressure (< 5 Pa); in a pressure range of 10-500 Pa for most plasma CVD, contribution of nanoparticles to the film volume is 10-60% and cannot be disregarded [1-3]. CVD plasma tends to have inherently spatiotemporal non-uniformity of its internal parameters mainly because of nanoparticles. Nanoparticles have long time constant of their nucleation and growth. They tend to be charged negatively and are trapped in plasma. Nanoparticles act as loss sites of electrons, ions, radicals, and nanoparticles; and hence they have great influence on non-uniformity of plasma parameters, deposition rate, and film qualities. Particularly, they tend to give nonlinear response of CVD plasma, such as hysteresis, to discharge power and pressure. We show a model which reproduces well such non-linear response, and contribution of nanoparticles is one of keys to realize uniformity of high quality films [4, 5]. There is plenty of room to improve qualities of plasma CVD films by paying attention to contribution of nanoparticles to the films.

Work partly supported by JSPS KAKENHI grant numbers 26246036 and 16K13922.

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9:40am **PS+AS-MoM5 Surface-driven CH_4 generation from CO_2 in Low-pressure Non-thermal Plasma**, ***Kazunori Koga***, *S. Toko, S. Tanida, M. Shiratani*, Kyushu University, Japan

The methanation of CO_2 attracts attention as the way to produce rocket propellant fuels at Mars because CO_2 comprises 95% of the atmosphere of Mars and water exists on Mars [1]. This reaction is called the Sabatier process and has been studied using catalysts under high pressure over 1 atm and high temperature above 200 ºC to realize a high conversion efficiency. However, the pressure on Mars is 135 times smaller than that of the Earth, and the average temperature is extremely low of -63 ºC [2]. A method using low-pressure non-thermal plasma allows methanation under low pressure and low temperature conditions [3]. Therefore, the plasma process is suitable for methanation at Mars. Here, we converted CO_2 to CH_4 using a capacitively coupled plasma (CCP) together with Cu catalyst. Experiments were carried out using a CCP reactor, excited at a frequency of 60 MHz. The electrode diameter was 50 mm and the distance between the electrodes was 6.1 mm. The electrode material was Cu. CO_2 gas flow rate was 1.0 sccm and that of H_2 was 6.0 sccm . The pressure was 750 Pa and the temperature was room temperature. The discharge power was set in a range of 10 to 100 W. Gas composition in the discharge plasmas was measured with a quadrupole mass spectrometer. CH_4 yield depends on surface condition of Cu electrodes, indicating that surface reactions on Cu electrodes dominate the CH_4 generation. Moreover, CH_4 generation has a long time constant more than 500 s, whereas CO_2 conversion has a short time constant of 80 s. These results indicate that CO_2 conversion takes place in gas phase by electron impact dissociation, while CH_4 generation involves several reaction steps. I will discuss the detail mechanisms at the conference.

Work supported partly by JAXA and JST.

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10:00am **PS+AS-MoM6 Plasma Modification of Carbon Fibres for Tough Carbon Fibre Composites**, ***Sally McArthur***, *R. Radjef, BL. Fox*, Swinburne University of Technology, Australia

Carbon-fibre manufacturing is a well established process that includes a surface treatment and a sizing step which are fast and easily incorporated into the production process. In the electrolytic oxidation steps, ammonium bicarbonate is used to introduce functional and polar groups to the surface while weakly bound basal planes are removed and the surface roughness is increased. All these are desired effects that are then covered with the application of the sizing layer, which protects the fibre surface during subsequent processing steps. The size is generally an epoxy based emulsion that provides handleability, lubrication, protection and is supposed to create a strong bond. This production process creates a complex multilayered interphase that is not well understood. It is believed that the size partially reacts with the surface functional groups, leaving a sizing layer that is depleted in epoxide groups and hence not able to fully cure. Furthermore how do we know that enough hardener diffuses through the matrix to the fibre surface to fully cure the sizing layer in the first place?

The aim of this study is to replace the current surface treatment and sizing step by a two-step plasma approach that allows the formation of a controlled interphase. In part one of this project a comparative study between electrolytic oxidation and air plasma treatment has been performed. In a second stage plasma polymerisation of TMDSO was used to produce films of variable mechanical properties by controlling the plasma power. This talk will focus on the the development and characterisation of the lab-based plasma system used to deposit uniform coatings onto the carbon fibres using a reel-to reel process and dual electrode array.

10:40am **PS+AS-MoM8 Damage Free Plasma Etching Processes of III-V Semiconductors for Microelectronic and Photonic Applications**, ***Erwine Pargon***, *M. Bizouerne, C. Petit-Etienne, L. Vallier, G. Gay, M. Fahed, K. Rovayaz, M. Fouchier, C. Bellegarde, V. Renaud, G. Cunge, O. Joubert*, CNRS-LTM, Université Grenoble Alpes, France, *E. Martinez, N. Rochat*, CEA-Leti, France **INVITED**

Due to their inherent advantages of direct bandgap and high electron mobility, III-V semiconductor materials are today widely used as active materials for a wide range of applications including high-speed and power electronic devices, and many types of opto-electronic and photonic devices. Recent progress in both molecular wafer bonding technology and monolithic heteroepitaxy let envisage the integration of III-V semiconductors directly on a Silicon platform. If successful, such integration paves the way for the emergence of highly performant devices, taking advantages of both III-V unique properties and the maturity of Si processing. Some promising examples are the use of high mobility III–V channel materials to extend the performance of Si CMOS, or the unification of electronics and photonics by combining photonic components with a silicon platform for next-generation optical interconnects. For all these future technologies, development of industrial processes for III-V semiconductors patterning is necessary. Plasma etching allows feature patterning with a nanometric control of the dimension, but one major drawback is the creation of defects in the vicinity of the etched surfaces, that can change the electro-optical properties of the semiconductor, and ultimately compromise the device performance. There is today a lack of knowledge on by which mechanisms and to what extent the plasma etching process induces damage at the III-V pattern sidewalls and the consequence it has on the device performance. The objective of this work is first to provide a better understanding of plasma-induced damage at the sidewalls of micro-nano-patterned III-V semiconductors by establishing a direct link between structural and chemical modifications induced by plasma etching, and opto-electrical properties. Based on such comprehensive know-how, the second objective is to provide technological solutions to minimize this damage in order to propose low damage plasma process compatible with the fabrication of commercial devices. The present study mainly focuses on the plasma etching process development of InGaAs used as a high mobility channel in a FinFET for microelectronic applications and of InGaAs/InP heterostructures used as a laser in hybrid photonic integrated circuits. Etching experiments are carried out in industrial ICP reactors. The structural damage induced at the pattern sidewalls (amorphization, stoichiometry, roughness..) are evaluated by electronic microscopies, AFM and nanoauger spectroscopy. The optical properties of the III-V semiconductors at the pattern sidewalls are analyzed by cathodoluminescence.

11:20am **PS+AS-MoM10 Fabrication of Metal Nanoparticle-dispersed Nanocomposite Films by *In Situ* Plasma Reduction of Metal Cation-containing Polymer Films**, *D.R. Boris,* Naval Research Laboratory, ***Souvik Ghosh****,* Case Western Reserve University, *S.C. Hernandez,* Naval Research Laboratory, *C.A. Zorman,* Case Western Reserve University, *S.G. Walton,* Naval Research Laboratory, *R.M. Sankaran,* Case Western Reserve University

Nanocomposites composed of inorganic nanoparticles and polymers have broad applications because of their unique combination of optical, electrical, thermal, and mechanical properties. A key fabrication challenge is dispersion of the two different phases which leads to separation and particle agglomeration. Compared to mixing premade nanoparticles with polymers, *in situ* formation of nanoparticles from a thin film containing the metal precursor and polymer has the potential to improve dispersion. Various approaches to reacting the metal precursor have been explored including heat treatment, UV exposure, and chemical processing. Low-temperature plasmas are particularly unique due to their inherent compatibility with temperature-sensitive polymers, and potential for rapid large-area processing. However, the mechanism for plasma-driven particle formation remains poorly understood.

Here, we carry out a systematic study of *in situ* plasma reduction of metal-cation containing polymer films to form nanoparticle-dispersed nanocomposites. Films were prepared from solutions of silver nitrate ($AgNO_3$) and polyacrylic acid (PAA). Chelation of the polymer with the metal cation produced a precipitate that was collected by centrifugation and cast as a thin film. The films were then exposed to a low-pressure, electron-beam generated plasma operating over a broad set of conditions aimed at delivering a controlled flux of low-energy argon ions. The as-treated films were analyzed with UV-visible absorbance spectroscopy and scanning electron microscopy (SEM). Absorbance confirms the presence of the localized surface plasmon resonance (LSPR) for Ag nanoparticles. The spectra show significant changes in the peak intensities with negligible shifts in the peak wavelength with plasma process changes, indicating that the particle concentration increases or decreases with a relatively constant average particle size. We correlated these changes in particle concentration to the variation in charge fluence at the film surface.

This work is partially supported by the Naval Research Laboratory base program and the National Science Foundation under Grant No. SNM-1246715.

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

New Imaging and Spectroscopy Methodologies

Moderators: Wonhee Ko, Oak Ridge National Laboratory, An-Ping Li, Oak Ridge National Laboratory

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Support by the European Commission under PAMS project (contract no. 610446) and by the Polish Ministry of Science and Higher Education (contract no. 0341/IP3/2016/74) are gratefully acknowledged.

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

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

We report on a new voltage spectroscopy technique applied to PFM that rapidly acquires dense 2D maps of local hysteretic material response. This technique combines the acquisition of the complete information about the cantilever response with intelligent signal filtering techniques to enable direct measurement of material strain in response to the probing bias. Our technique enables precise spectroscopic imaging of the polarization switching phenomena 3,500 times faster than currently reported methods. By rapid acquisition of a large number of hysteretic loops on very dense grids, this technique will enable significant insight into nanoscale polarization dynamics and phenomena such as polarization fatigue or local wall displacements that remain difficult to study at the desired spatial and temporal scales, and are crucial for integration of ferroelectric nanostructures in future electronic devices.

This research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.

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

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

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

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

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

Surface Science Division
Room: 25 - Session SS+AS+MI-MoM

Organic/Inorganic Surfaces and Interfaces
Moderators: Liney Arnadottir, Oregon State University, Bruce Koel, Princeton University

8:20am **SS+AS+MI-MoM1 The Use of EC-STM to Study the Nanoscale Structure and Behavior of Atomically Thin Ag Films on Au Surfaces**, *J.A. Phillips, H.R. Morgan, L.E. Jackson, G. LeBlanc,* ***Erin Iski***, University of Tulsa **INVITED**

The formation of an atomically thin Ag monolayer on a Au(111) surface has been shown to significantly alter the properties of the underlying substrate (1). A further exploration into the chemical mechanisms by which these thin films are deposited reveals two different sources of Ag during the formation of the monolayer. Electrochemical Scanning Tunneling Microscopy (EC-STM) and Cyclic Voltammetry (CV) are used to probe the *in-situ* interfaces of these systems. EC-STM is a unique technique in that in addition to providing a local probe of the atomic surface structure, EC-STM also functions as a 3-electrode cell in which redox chemistry can be performed to understand the chemical reactivity of the surface. Also, cyclic voltammograms (CVs) can be generated to provide specific information regarding the nature of the redox events occurring at the surface. In addition to the ability to perform two kinds of Ag Underpotential Deposition (UPD) on Au(111) using a single solvent system (AgCl), this investigation also includes the examination of the effect of different halides on the thermal stability of the as-formed Ag monolayers. While it has been previously demonstrated that deposition from a AgCl system affords oxidative and thermal stability up to 1,000 K (1), the role of the identity of the halide has yet to be explored, specifically comparing depositions from both AgBr and AgI solutions. Preliminary investigations indicate that a monolayer formed from the AgBr system remains on the surface after the 1,000 K thermal treatment, while the same is not true for the AgI system. The origin of these differences will be examined in detail with EC-STM, CVs, and Density Functional Theory (DFT). Studies of this nature are critical to understanding the fundamental mechanisms behind thin film growth using UPD and the exact role of halides in the observed thermal stabilization. The ability to experimentally choose different surface properties based on electrochemical parameters and solution composition during deposition could lead to exciting new directions for thin film technologies.

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9:00am **SS+AS+MI-MoM3 Decomposition and Self-Assembly of Coronene on Pt(111)**, ***Chen Wang***, University of California Irvine, *K. Thurmer, N. Bartelt*, Sandia National Laboratories

Composed of seven benzene rings that form a larger, hexagonal structure, coronene is a molecule often referred to as “the smallest flake of graphene”. As such, this molecule provides insight into the nature and dominance of edge effects in graphene-based systems and devices. Furthermore, as a polynuclear aromatic hydrocarbon, coronene serves as a common chemical precursor and building block in soot formation, a process that is still largely mysterious in its earliest stages. This work presents the study of coronene assembly on Pt(111) at the nanoscale by using scanning tunneling microscopy and density functional theory calculations. Both experimental and theoretical methods focus on understanding the intramolecular interactions between neighboring molecules of coronene and with the underlying metal substrate by characterizing the molecular assembly at the monolayer and bilayer. At the monolayer, the platinum surface is highly interactive with the coronene, resulting in fragmentation of the molecule on and a high binding energy to the platinum surface. At the bilayer, platinum interference is screened, and several coronene-based structures are observed. In situ annealing allows for the observation of molecular clustering as the surface dewets. The coronene molecules first form chains, then clumps, and finally large clusters which bear notable resemblance to incipient soot. These findings are promising contributions to soot research and further general understanding of graphene at its the smallest scale.

9:20am **SS+AS+MI-MoM4 Understanding of Single-layer ZnS Supported on Au(111)**, ***Xingyi Deng***, *D.C. Sorescu, J. Lee*, National Energy Technology Laboratory

We investigate the structure and energetics of ZnS single-layer supported on Au(111) using a combination of experimental and theoretical approaches. Single-layer of ZnS, consisting of one atomic layer of ZnS(111) plane, has been grown on Au(111) via sulfurization of metallic Zn in H_2S at T = 550 K. ZnS single-layer on Au(111) forms a ZnS-(3 × 3)/Au(111)-(4 × 4) coincidence structure based on the LEED measurement. High resolution STM images reveal hexagonal unit cells of 6.7 × 6.7 $Å^2$ and 11.6 × 11.6 $Å^2$, corresponding to √3 and 3 times the unit cell of the ideal zincblende ZnS-(1 × 1), respectively, depending on the tunneling conditions. A significantly reconstructed non-planar structure of ZnS single-layer is suggested based on density functional theory (DFT) calculations. Specifically, 2/3 of the S anions are found to be located nearly in the plane of the Zn cations and the rest 1/3 of the S anions protruding above the Zn plane. These results are discussed and compared with other related systems, such as ultrathin ZnO supported on Au(111), in order to advance our understanding of materials in the ultrathin regime.

9:40am **SS+AS+MI-MoM5 X-ray Microscopy and Spectroscopy Insights of Metal-Organics Contacts**, ***Der-Hsin Wei***, *K.T. Lu, T.H. Chuang, C.I. Lu, Y.J. Hsu*, National Synchrotron Radiation Research Center, Taiwan, Republic of China

Abstract

After the giant magnetoresistance (GMR) was demonstrated in Co/Alq_3/LSMO trilayers [1], the rise of organic spintronics was no longer a question of if, but when. Latter it was even suggested that the interfaces are the most critical players toward the success of organic spinronics [2]. Unfortunately, despite much effort, vertical organic spin valve (OSV) could not establish a meaningful GMR at room temperature unless a thin insulator film is inserted between the ferromagnetic electrode and organic spacer [3-5]. Calls for spectroscopic studies were thus made to improve or even scrutinize the existing understandings [6]. In this report, I describe a jointed X-ray microscopy and spectroscopy investigations on multiple ferromagnet-organic hybrid structures including Co/pentacene, Fe/C_{60}, Co/C_{60}, and Ni/C_{60}. Our study indicates that the ferromagnetic (FM) 3*d* transition metals land on organic semiconductor (OSC) films suffer an apparent magnetization retardation. Further investigation reveals that there is more than a reactive interface behind the scenes. Finally, the connection between our findings and reported transport measurements is addressed.

Acknowledgments

Financial supports from Minister of Science and Technology (MoST) and National Synchrotron Radiation Research Center at Taiwan are greatly acknowledged.

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10:00am **SS+AS+MI-MoM6 Anchoring of Carboxylic and Phosphonic Acids on Atomically Defined Oxide Surfaces: The Role of Protons, Hydroxyl Groups and Water**, *M. Schwarz, T. Xu, S. Mohr, C. Schuschke,* ***Joerg Libuda***, University Erlangen-Nuernberg, Germany

Organic-oxide interfaces are at the heart of various emerging technologies, ranging from organic electronics to solar energy conversion. Their functionality arises from complex organic layers which are normally anchored to the oxide surface via specific linker groups. Typically, the anchoring groups release protons, thus forming surface hydroxyl groups. The role of these protons, the surface hydroxyl groups, and the interfacial water is one the most essential but, simultaneously, also one of the most poorly understood aspects in organic film formation.

We studied the interaction of water, carboxylic acids, and organic phosphonic acids with different cobalt oxide surfaces, namely Co_3O_4(111), CoO(111) and CoO(100), prepared in form of thin well-ordered films on Ir(100). The interaction of water with these surfaces is strongly structure-dependent and ranges from weak molecular adsorption on CoO(100) to the formation very strongly bound OH groups on Co_3O_4(111). Similarly, pronounced structure dependencies are observed upon anchoring of benzoic acid. Time-resolved and temperature-programmed vibrational spectroscopies with deuterated carboxylic acids indicate the formation of well-defined mixed adsorbate layers consisting of bridging benzoates and OD groups formed in the anchoring reaction. For phthalic acid, which may bind via one or via two linker groups, the adsorption geometry is controlled by the arrangement of the surface Co^{2+} ions. Organophosphonic acids, on the other hand, show a complex temperature-dependent anchoring behavior, which originates from the multiple adsorption geometries which these molecules can adopt. Finally, we investigated the anchoring behavior of larger organic species, such as carboxylated porphyrin derivatives, for which differently oriented phases can be observed by time-resolved in-situ spectroscopy during organic film growth in UHV. Intriguingly, the same reactions can also be monitored by in-situ vibrational spectroscopy at the solid/liquid interface on the same oxide surfaces prepared in UHV. We present first spectroscopic data, in which we directly compare these anchoring reactions in UHV and at the solid/liquid interface.

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10:40am **SS+AS+MI-MoM8 Thiolate *versus* Selenolate: Structure, Binding Strenght, Thermal Stability, and Charge Transfer Properties**, *J. Ossowski,* Jagiellonian University, Poland, *T. Wächter,* Universität Heidelberg, Germany*, T. Żaba,* Jagiellonian University, Poland*, L. Silies, M. Kind,* Universität Frankfurt, Germany*, A. Noworolska,* Jagiellonian University, Poland, *F. Blobner,* Technische Universität München, Germany, *D. Gnatek, J. Rysz,* Jagiellonian University, Poland, *M. Bolte,* Universität Frankfurt, Germany, *P. Feulner,* Technische Universität München, Germany, *A. Terfort,* Universität Frankfurt, Germany, *M. Zharnikov,* Universität Heidelberg, Germany, ***Piotr Cyganik***, Jagiellonian University, Poland

Selenolate is considered as an alternative to thiolate to serve as a headgroup mediating the formation of self-assembled monolayers (SAMs) on coinage metal substrates. There are however ongoing vivid discussions regarding the advantages and disadvantages of these anchor groups, regarding, in particular, the energetics of the headgroup-substrate interface, thermal stability and their efficiency in terms of charge transport/transfer. Here we introduce a well-defined model system of 6-cyanonaphthalene-2-thiolate and -selenolate SAMs on Au(111) to resolve these controversies. The exact structural arrangements in both types of SAMs are somewhat different, suggesting a better SAM building ability in the case of selenolates [1]. At the same time, both types of SAMs have similar packing densities and molecular orientations [1]. This permitted reliable competitive exchange and ion beam induced desorption experiments which provided an unequivocal evidence for a stronger bonding of selenolates to the substrate as compared to the thiolates [1]. The thermal analysis reveals higher stability of thiolates as compared to selenolates due to the higher stability of the S-C bond as compared to the Se-C which results from stronger bonding of selenolates with the Au(111) substrate [2]. Regardless of these differences, the dynamic charge transfer properties of the thiolate and selenolate based adsorbates were found to be identical as determined by the core-hole-clock approach, which is explained by a redistribution of electron density along the molecular framework, compensating the difference in the substrate-headgroup bond strength [1].

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[2] Ossowski J. *et al* paper in preparation.

11:00am **SS+AS+MI-MoM9 Preserving Material Morphology by Gas-Phase Functionalization: Surface Modification of ZnO with Propiolic Acid**, *F. Gao,* University of Delaware, *S. Aminane,* Université Pierre et Marie Curie, France, *S. Bai,* ***Andrew Teplyakov***, University of Delaware

Chemical functionalization of ZnO surface is commonly performed using reactions of carboxylic acids with the surface of this material. However, liquid phase reactions of carboxylic acids with ZnO often cause changes in surface morphology. Etching has been widely acknowledged as a potential problem in this functionalization process. This work will use gas-phase propiolic acid dosed in vacuum to modify ZnO nano-powder while preserving its morphology and leaving the alkyne group available for subsequent chemical modification via the azide‒alkyne cycloaddition “click” reaction with benzyl azide. The formation of the surface carboxylate following gas-phase exposure of propiolic acid is shown to be a highly selective process confirmed by solid-state nuclear magnetic resonance spectroscopy, Fourier-transform infrared spectroscopy, and X-ray photoelectron spectroscopy. Electron microscopy is used to confirm that the morphology of the material is not affected during this modification and to compare with the liquid phase processing. It is also found that ZnO surface is stabilized by propiolic acid, as following this initial modification, further secondary postmodification based on either gas-phase exposure or liquid phase reactions were tested and confirmed to not affect the morphology of ZnO material. Based on this functionalization approach, delicate nanostructures, nanorods, or nanopowders and even ZnO-based devices can be chemically modified for further functionalization for applications where preserving surface morphology during chemical modification is especially important.

11:20am **SS+AS+MI-MoM10 Enhanced Long-range Magnetic Order by the Organic-Ferromagnetic Hybrid Interface**, ***Yao-Jane Hsu***, *M.W. Lin,* National Synchrotron Radiation Research Center, Taiwan, Republic of China, *P.H. Chen,* National Tsing-Hua University, Taiwan, Republic of China, *Y.L. Lai,* National Synchrotron Radiation Research Center, Taiwan, Republic of China, *T.N. Lam,* National Chiao-Tung University, Taiwan, Republic of China, *D.H. Wei, H.J. Lin, Y.Y. Chin,* National Synchrotron Radiation Research Center, Taiwan, Republic of China, *J.H. Wang,* National Taiwan Normal University, Taiwan, Republic of China

The interplay between ferromagnetic and organic layers critically affects the efficiency of spin filtering in the organic/molecular spintronics. The hybridized properties at organic-ferromagnetic heterostructure is hence important. We investigated the spin interface in terms of the electronic structure and magnetic coupling of tetrafluorotetracyanoquinodimethane (F4-TCNQ) on nickel (Cu(100)/Ni) surface. The experimental results display magnetic hardening upon F4-TCNQ adsorbed on Ni surface. This enhanced magnetic ordering after molecular tailoring was studied by the surface-sensitive and element specific X-ray Magnetic Circular Dichroism (XMCD). The XMCD reveals that the orbital and spin moment of Ni is significantly increased on the in-plane, while that keep almost unaltered at out-of-plane. Through the strong superexchange coupling at in-plane surface, the nonmagnetic F4-TCNQ is spin polarized. Additionally, we found the enhanced magnetic ordering expressed larger domain sizes and less domain boundary from the measurements of surface magnetic anisotropy performed by magneto-optical Kerr effect (MOKE) and the magnetic domains inspected by photoelectron-emission microscope (PEEM). It suggests that the enhanced long-range magnetic order of organic-ferromagnetic interface is an effective spin filtering for constructing high efficient organic spintronics.

11:40am **SS+AS+MI-MoM11 Interaction of Coronene with Mo-C$_{60}$ Nanospheres: The Effects of Substrate Curvature on Molecular Adsorption**, ***Nathaniel W. Kabat***, *E. Monazami, P. Reinke,* University of Virginia

Surface curvature has been observed to effect molecular adsorption, but little systematic work has been done in the regime where substrate corrugation is the same magnitude as molecule size. Here we present a scanning tunneling microscopy/spectroscopy (STM/STS) study of the interaction between molybdenum-fullerene nanospheres and coronene molecules. The nanospheres template is formed by a solid-state reaction between Mo thin films and a fullerene layer which is triggered by an annealing step. The reaction between the fullerenes and molybdenum breaks the symmetry of a fullerene layer but retains a dense molecular packing of visibly distorted fullerene-like structures. The electronic structure and bandgap of the nanospheres can be adapted by annealing and is driven by substitutional metal atom incorporation in the C$_{60}$. The interaction of coronene molecules with a gold surface serves as a model system representing the limiting case of a flat metallic surface and indicates that the molecular height varies with annealing temperatures while still exhibiting long range order. We will present coronene adsorption on nanospheres from wide bandgaps (2 eV) to fully metallic surfaces and discuss the adsorption geometries of coronene. We do not observe long range order of coronene molecules on the nanospheres surface, indicating that the localized nanosphere curvature has a strong influence on the absorption geometry. These results provide the beginning steps of understanding the ways in which nanosphere-molecule interaction can be controlled by the localized surface curvature. We acknowledge the support from the National Science Foundation award CHE-1507986 by the Division of Chemistry (Macromolecular, Supramolecular and Nanochemistry).

Tandem MS Focus Topic
Room: 5 & 6 - Session TM+AS-MoM

New Instrumentation Featuring Tandem MS

Moderators: Chris Anderton, Pacific Northwest National Laboratory, Daniel Graham, University of Washington

8:20am **TM+AS-MoM1 *In Situ* MS/MS Analysis on Biological Samples using Imaging Secondary Ion Mass Spectrometry (SIMS)**, ***Hua Tian***, Pennsylvania State University **INVITED**

SIMS imaging allows characterization of biomaterials with high lateral resolution. The method has not, however, yet gained popularity within the biological community. One reason is the need for MS/MS analysis due to isobaric interferences associated with the complex composition of biomaterials. Although MS/MS has been routine in imaging mass spectrometry (IMS) with matrix assisted laser desorption ionization (MALDI), it is rarely incorporated with SIMS imaging. Until recently, only a few SIMS instruments had the capability of tandem or parallel MS/MS imaging, for example the J105 3D Chemical Imager, PHI nanoTOF II and IonToF Orbitrap Hybrid [1-3]. The identification of lipids and metabolites in various biosystems, such as Drosophila brain section[4], Zebra Finch brain section, Zebrafish whole body section[1] and bacteria [2], has been reported so far. The precise precursor selection, high lateral resolution and high energy collisional fragmentation are the must-have for the design of new instrumentation for MS/MS capability. Gas cluster ion source (GCIB) is also a necessity for generating sufficient precursor ions especially at extended mass range of SIMS spectra, allowing for a much greater variety of biomolecule studies. Here, we present a review of the current state of MS/MS in SIMS, and illustrate the power of this technique using a hybrid mass spectrometer that employs shaped field bunching for injection into the collision cell. The possibility to utilize laser-induced photo-fragmentation in this instrument is also discussed.

1. Fisher, G. L.; Bruinen, A. L.; Ogrinc Potočnik, N.; Hammond, J. S.; Bryan, S. R.; Larson, P. E.; Heeren, R. M. A., A New Method and Mass Spectrometer Design for TOF-SIMS Parallel Imaging MS/MS. *Analytical Chemistry* **2016,***88* (12), 6433-6440.

2. Wehrli, P. M.; Lindberg, E.; Angerer, T. B.; Wold, A. E.; Gottfries, J.; Fletcher, J. S., Maximising the potential for bacterial phenotyping using time-of-flight secondary ion mass spectrometry with multivariate analysis and Tandem Mass Spectrometry. *Surf Interface Anal* **2014,***46*, 173-176.

3. Hybrid SIMS. https://www.iontof.com/hybrid-sims-ms-ms-organic-mass-spectrometry-surface-analysis.html (accessed April 28, 2017).

4. Phan, N. T. N.; Munem, M.; Ewing, A. G.; Fletcher, J. S., MS/MS analysis and imaging of lipids across Drosophila brain using secondary ion mass spectrometry. *Analytical and Bioanalytical Chemistry* **2017**, 1-10.

9:00am **TM+AS-MoM3 Molecular Depth Profiling with a New Hybrid SIMS Instrument for Improved Molecular Identification using Tandem MS**, ***Alexander Pirkl****, R. Moellers, H.F. Arlinghaus, J. Zakel, D. Rading, E. Niehuis*, ION-TOF GmbH, Germany

The characterisation of organic layer systems is of increasing interest in many research areas. Since the application of large argon clusters as sputter species in SIMS, depth profiling of almost all organic materials has become feasible whilst retaining the intact molecular information during the profile.

However, molecular identification of unknown substances, e.g. contaminants, can be hampered by constraints in mass resolution and mass accuracy of a standard TOF analyser. To overcome this problem, we have developed a new Hybrid SIMS instrument, which uniquely combines all advantages of a state-of-the-art TOF-SIMS with the mass spectrometry performance of an Orbitrap mass analyzer (Q Exactive^{TM} HF) [1]. The Q Exactive mass spectrometer provides a mass resolution of more than 240,000 @ m/z = 200, sub ppm mass accuracy, and fully integrated MS/MS capabilities that allow low energy collision induced fragmentation for structural analysis of complex molecules. All in all this dramatically increases the level of confidence for the SIMS analysis.

In this contribution, we will present the new instrument and discuss applications from various fields including organic electronics. We will demonstrate how the extremely high mass resolution of the Q Exactive mass spectrometer can be advantageously used to resolve mass interferences which cannot be separated in a standard TOF-SIMS instrument. We will also show examples of structural analysis using the high-performance MS/MS capabilities and discuss the new possibilities of the unique TOF / Q Exactive mass spectrometer combination.

[1] Passarelli et al, The 3D OrbiSIMS – A new Method for Label-Free Metabolic Imaging with Sub-cellular Lateral Resolution and High Mass Resolution, submitted 2017.

9:20am **TM+AS-MoM4 Spatially-resolved Tandem Mass Spectrometry Increases Molecular Confidence in a Multimodal Mass Spectrometry Imaging Investigation of a Tripartite Plant-fungus-cyanobacteria Interaction**, ***Dušan Veličković****,* Pacific Northwest National Laboratory*, A.A. Carrell,* Duke University*, R.K. Chu,* Pacific Northwest National Laboratory*, D. Pelletier,* Oak Ridge National Laboratory*, L. Paša-Tolić,* Pacific Northwest National Laboratory*, D.J. Weston,* Oak Ridge National Laboratory*, C.R. Anderton*, Pacific Northwest National Laboratory

Plant microbiomes represent a complex mix of interacting species with diverse physiologies and phylogenetic origins. Their functional outcomes are critical to biogeochemical cycles, yet measuring molecular (e.g., metabolite) exchange among interacting species is a major technical challenge. Traditional bulk metabolomic technologies are often limited in their ability to distinguish between molecules that remain localized within microbes and exuded molecules that are in proximity, thus often disregarding the multifaceted chemical exchange within and between interacting species. Mass spectrometry imaging (MSI) methodologies have been recently adopted to visualize the flow of metabolites produced by agar-supported microbial colonies. Several ionization modalities are suitable for MSI of microbial communities, with matrix-assisted laser desorption/ionization (MALDI) being most commonly used. When coupled with ultra-high resolution mass analyzers (e.g., Fourier transform ion cyclotron resonance mass spectrometers; FTICR-MS), these imaging sources offer the high mass resolution and accuracy needed for putative identification of metabolites in individual pixels in the image. However, orthogonal methodologies (e.g., tandem MS) are often required for confident metabolite identification.

Herein, we explored the interactions within a tripartite system of moss, cyanobacteria, and fungus using a multimodal imaging strategy, which employs liquid extraction surface analysis (LESA) tandem MSI to examine previously MALDI imaged samples. This method improved exometabolite identification confidence by preserving spatial dimensionality in the tandem MS experiment. Specifically, we found the combination of these two imaging modalities generated very congruent mass spectral information, providing the link between highly accurate structural information offered by LESA and high spatial resolution attainable by MALDI. Finally, FTICR-based secondary ion mass spectrometry provided new insights into tripartite community using correlative fragment data (SIMS and LESA-MS/MS), while delivering higher lateral resolution MS images. These multimodal imaging results offer detail metabolic insights into a moss, cyanobacterium, and fungus in isolation and when in a tripartite symbiosis.

9:40am **TM+AS-MoM5 The Biosynthesis of Protective Metabolites in Amazonian *Sextonia rubra* Revealed by 100 nm-Scale TOF-SIMS Tandem MS Imaging**, ***Gregory L. Fisher***, Physical Electronics, *T. Fu, D. Touboul,* Institut de Chimie des Substances Naturelles, CNRS, France*, S. Della-Negra,* Institut de Physique Nucléaire, CNRS, France*, E. Houël, N. Amusant, C. Duplais,* Cirad, UMR EcoFoG, AgroParisTech, CNRS, INRA, France*, A. Brunelle*, Institut de Chimie des Substances Naturelles, CNRS, France

We have explored the botanical synthesis of bioactive molecules in the wood of *S. rubra* (Figure 1) via TOF-SIMS Parallel Imaging MS/MS. This investigation is part of an effort to develop a new strategy for investigating natural product formation in relation to the secondary metabolite synthesis during heartwood formation. The TOF-TOF tandem mass spectrometer of the PHI *nanoTOF* II enabled, for the first time in this field of study, simultaneous surface screening of the botanical matrix chemistry by TOF-SIMS (MS^1) imaging and targeted identification of biosynthetic components by MS/MS (MS^2) imaging [1]. Imaging of molecules with unambiguous identification occurred in minutes without observable degradation of the specimen. Hence, the wood chemistry was broadly profiled while multiple tandem MS imaging analyses were performed for discovery.

The metabolites of rubrynolide and rubrenolide, having significant xylophage toxicity and antifungal properties [2], are produced in oil cells that are found in close proximity to both vessels and parenchyma cells. Moreover, there are thought to be several bio-molecular precursors en route to these bioactive metabolites. Our goal was to identify biosynthetic precursors, and to verify their coincidence with rubrynolide and rubrenolide, via tandem MS imaging. We were able to demonstrate the presence of numerous precursors and to confirm or derive their structure using the tandem MS product ion spectrum, thus contributing in the exploration of natural product biosynthesis.

[1] (a) G.L. Fisher, A.L. Bruinen, N. Ogrinc Potočnik, J.S. Hammond, S.R. Bryan, P.E. Larson, R.M.A. Heeren, *Anal. Chem.* **2016**, DOI: 10.1021/acs.analchem.6b01022. (b) G.L. Fisher, J.S. Hammond, P.E. Larson, S.R. Bryan, R.M.A. Heeren in *SIMS XX Proceedings* (Ed.: D. Castner), Wiley, New Jersey, **2016**, DOI: 10.1116/1.4943568.

[2] (a) A.M.S. Rodriguez, P.N.E.T. Theodoro, V. Eparvier, C. Basset, M.R.R. Silva, J. Beauchêne, L.S. Espíndola, D. Stein, *J. Nat. Prod*. **2011**, DOI: 10.1021/np1001412. (b) A.M.S. Rodriguez, N. Amusant, J. Beauchêne, V. Eparvier, N. Lemenager, C. Baudasse, L.S. Espíndola, D. Stein, *Pest Manag. Sci*. **2011**, DOI: 10.1002/ps2167.

10:40am **TM+AS-MoM8 Metabolite Annotation for Ultra-HR Imaging Mass Spectrometry: MS1 and Beyond**, ***Theodore Alexandrov***, European Molecular Biology Laboratory, Germany **INVITED**

Metabolite imaging mass spectrometry promises to localize small molecules, metabolites, and lipids in tissues, microbial and cell cultures, and to interpret them in the context of cellular heterogeneity. However, just until recently the molecular interpretation of the big data generated by this technique was hampered by the lack of bioinformatics for metabolite identification. We recently developed and implemented a bioinformatics approach that allowed us to identify hundreds of metabolites from hundreds of datasets from various biological systems. We will present how this big data mining approach helps extract molecular knowledge from terabytes of imaging mass spectrometry data, find the link between metabolism and disease, and picture metabolites across hundreds of datasets.

11:20am **TM+AS-MoM10 Multivariate Analysis of combined ToF-SIMS and Orbitrap-SIMS data**, ***Henrik Arlinghaus***, *M.R. Keenan, A. Pirkl, R. Moellers, E. Niehuis*, ION-TOF GmbH, Germany

Advances in SIMS instrumentation, such as the advent of gas cluster ion sources, have greatly increased the analysis capabilities on organic samples, e.g. by reducing molecular fragmentation. However, the identification of molecules may still be limited by the mass resolution and mass accuracy of the analyzer. A Hybrid SIMS instrument[1], combining a ToF-SIMS mass analyzer and an Orbitrap^{TM} mass analyzer (Q Exactive^{TM} HF) has been developed in order to overcome these limitations, combining the high lateral and depth resolution and repetition rate of the ToF-SIMS analyzer with the high mass resolution, mass accuracy, and MS-MS capabilities of the Q Exactive HF analyzer (240,000 @ m/z = 200, sub ppm accuracy). This instrument generates a vast amount of data, rendering manual analysis of the full dataset impractical.

Multivariate analysis (MVA) may be used to reduce complex datasets to a small set of relevant factors, simplifying data interpretation. Established multivariate techniques, such as principal component analysis (PCA), have been used to analyze everything from a small set of inorganic spectra to complex three dimensional organic samples consisting of hundreds of millions of voxel spectra, such as OLEDs. These techniques are now routinely used for ToF-SIMS data analysis in many laboratories.

We will present results of multivariate analysis of datasets acquired using a Hybrid SIMS instrument, where we simultaneously analyzed both the ToF-SIMS and Orbitrap-SIMS data. This type of analysis presents unique challenges, such as contending with vastly different detector technologies and the corresponding differences in noise characteristics.

[1] Passarelli et al, The 3D OrbiSIMS – A new Method for Label-Free Metabolic Imaging with Sub-cellular Lateral Resolution and High Mass Resolution, submitted 2017.

Actinides and Rare Earths Focus Topic
Room: 22 - Session AC+AS+SA+SU-MoA

Chemistry and Physics of the Actinides and Rare Earths
Moderator: David Shuh, Lawrence Berkeley National Laboratory

1:40pm **AC+AS+SA+SU-MoA1 Oxidation and Crystal Field Effects in Uranium**, ***James G. Tobin***, University of Wisconsin-Oshkosh, *S.W. Yu*, Lawrence Livermore National Laboratory, *C.H. Booth*, Lawrence Berkeley National Laboratory, *T. Tyliszczak,* Lawrence Berkeley Lab, University of California, Berkeley, *D.K. Shuh*, Lawrence Berkeley National Laboratory, *G. van der Laan*, Diamond Light Source, UK, *D. Sokaras, D. Nordlund, T.C. Weng*, Stanford Synchrotron Radiation Lightsource, *P.S. Bagus*, University of North Texas

An extensive investigation of oxidation in uranium has been pursued. [1] This includes the utilization of soft x-ray absorption spectroscopy, hard x-ray absorption near-edge structure, resonant (hard) x-ray emission spectroscopy, cluster calculations, and a branching ratio analysis founded on atomic theory. The samples utilized were uranium dioxide (UO_2), uranium trioxide (UO_3), and uranium tetrafluoride (UF_4). A discussion of the role of nonspherical perturbations, i.e., crystal or ligand field effects, will be presented. The conclusions are as follows. (1) The hypothesis of the potential importance of CF effects in the XAS branching ratio (BR) analysis of 5f states was incorrect. (2) Both UO_2 and UF_4 are $n_{5f} = 2$ materials. The combination of the 4d XAS BR and RXES analyses is particularly powerful. (3) CF broadening in the L_3 RXES spectroscopy does not preclude a successful analysis. (4) The prior experimental result that n_{5f} (UO_2) = 3 and the proposed causation by covalent bonding was incorrect. UO_2 is an n5f = 2 material and analysis within a simple, ionically localized picture provides the correct result. (5) UO_3 appears to be an $n_{5f} = 1$ material. (6) While the 4d XAS BR analysis is blind to CF effects, crystal field and covalence remain important. (7) For localized actinide systems, the 4d XAS BR analysis founded upon the utilization of the intermediate coupling scheme remains a powerful tool. (8) For delocalized actinide systems, the BR analysis is problematic.

[1] J. G. Tobin, S.-W. Yu, C. H. Booth, T. Tyliszczak, D. K. Shuh, G. van der Laan, D. Sokaras, D. Nordlund, T.-C. Weng, and P. S. Bagus, Phys. Rev. B **92**, 035111 (2015)

2:00pm **AC+AS+SA+SU-MoA2 Electron Spectroscopy Studies of U and U-Mo Hydrides**, ***Ladislav Havela***, *M. Paukov, M. Dopita, L. Horak, M. Divis, I. Turek,* Charles University, Prague, Czech Republic, *T. Gouder, A. Seibert, F. Huber*, European Commission, Joint Research Centre, Karlsruhe, Germany, *D. Legut*, VSB - Technical University of Ostrava

U hydride was the first material indicating that 5*f* states can yield ferromagnetism analogous to 3*d* metals. However, the electronic structure of UH_3 is not yet well understood, and it is not clear to which extent it can be described by conventional band structure calculations. We have been studying structure and electronic properties of UH_3 and $(UH_3)_{1-x}Mo_x$ films synthesized by reactive sputtering. Primary diagnostics was performed by in-situ XPS. The U-4*f* core level spectra exhibit a development as a function of partial pressure of H_2 in Ar ($p_{Ar} = 8*10^{-3}$ mbar). Their intensity gradually decreases, they shift by 0.2 eV towards higher binding energies (BE) and an extended (9 eV wide) satellite structure develops on the high BE side of both 4*f* peaks. This tendency saturates at 5% H_2 concentration, and we assume that this pressure is sufficient to form UH_3. XRD and X-ray reflectivity proved indeed the β-UH_3 structure of deposited films, which were polycrystalline, but highly textured. Ferromagnetism of the UH_3 films has the correct Curie temperature $T_C \approx 165$ K. Magnetic coercivity of the films is enormous, the width of hysteresis loop exceeds 10 T at low temperatures. Details of the valence band observed in UPS reveal a transformation of the triangular emission of the U metal into a sharp feature at the Fermi level accompanied by a broad shoulder around 0.5 eV for the hydride. A distinct development was noticed also for the U-6*p* states, which become narrower and shift by 1.2 eV to higher BE in the hydride, which can be interpreted as an impact charge transfer from U towards H. Besides photoelectron spectroscopy, the variations of electronic states were monitored also by BIS spectra collected for the 1486.6 eV photon energy. The spectroscopy results are confronted with different types of in-initio calculations.

As U-Mo alloys tend to form nanocrystalline β-UH_3 based hydrides, we were curious about reactive sputter deposition of the U-Mo alloys. We found that the tendency to form hydrides is fast suppressed by Mo for room temperature sputtering (γ-U alloy without H is the product), but cooling the substrate to 77 K helps to maintain the hydride phase even for even higher Mo concentrations.

This work was supported by the Czech Science Foundation under the grant No. 15-01100S.

2:20pm **AC+AS+SA+SU-MoA3 Comparative Structural Studies of Tetravalent f ions in Solids and in Aqueous Solutions**, ***Lynda Soderholm***, Argonne National Laboratory **INVITED**

Predicting a metal ion's aqueous chemistry – including its stability, reactivity, and solubility – requires molecular-level knowledge of the various factors influencing speciation and complex formation. This chemistry is particularly complicated for f-ions, where the electrostatic, non-directional bonding provides flexibility to their coordination environments, which can vary widely depending on the ligating species. This presentation will focus on our efforts to establish trends in f-ion solution behavior and to provide a direct link between metal correlations in solution and the thermodynamic stability constants that are used to derive relative free energies of available metal-ligand complexes. Although several examples will be provided, the discussion will center on a comparison between the behaviors of tetravalent Th, Pu, and Ce and how differences in the complexes formed in solution impact the composition and structure of precipitates that form. High-energy X-ray scattering (HEXS) experimental results will be used to demonstrate how changing conditions can influence solution chemistry, with a specific emphasis on the role of the anion. X-ray surface-based techniques will be used to provide a link between solution speciation and the complexes that form on mineral surfaces. The structures of molecular species isolated as single-crystals from these solutions will be directly compared with the solution and surface-adsorbed species. This work is supported by the U.S. Department of Energy, Office of Basic Energy Science, Division of Chemical Sciences, Biosciences and Geosciences, Heavy Element Chemistry, under contract No. DE-AC02- 06CH11357.

4:00pm **AC+AS+SA+SU-MoA8 Interfacial Dynamics in Radiation Environments and Materials: An Energy Frontier Research Center**, ***Sue Clark***, Pacific Northwest National Laboratory **INVITED**

The US Department of Energy's Office of Environmental Management (EM) is faced with remediating millions of liters of highly radioactive wastes that resulted from the production of nuclear weapons during the Cold War. These legacy wastes are stored in large, underground tanks at former nuclear weapons production sites in the US. Not only are these wastes radioactive, but they are also highly alkaline and concentrated in electrolytes. Using currently available technologies and approaches. EM estimates that processing these wastes into waste forms for disposal in a geologic repository will take at least 5 decades and over $300 billion dollars. Basic research on the chemical and physical behavior of these materials in such extreme conditions is needed to provide a foundation of innovation to accelerate processing and reduce aggregate costs.

IDREAM is an Energy Frontier Research Center (EFRC) conducting fundamental research to support innovations in processing high-level radioactive wastes (HLW). Activities in IDREAM are designed to support the transformation of HLW processing by elucidating the basic chemistry and physics required to control and manipulate interfacial phenomena in extreme HLW environments (e.g., non-equilibrium, heterogeneous, and chemically complex). This foundational knowledge is required to achieve IDREAM's vision to master molecular–to–mesoscale chemical and physical phenomena at interfaces in complex environments characterized by extremes in alkalinity and low-water activity, and driven far from equilibrium by ionizing (g,b) radiation. Further, understanding these processes will enable prediction of waste aging over the many decades required to complete this difficult cleanup task.

Currently, IDREAM activities focus on the aluminate anion in alkaline solutions, and its nucleation into boehmite (aluminum (oxy)hydroxide, AlO(OH)) and gibbsite (aluminum hydroxide, $Al(OH)_3$) , as they are key principal components of bulk waste materials to which a variety of other metal ions and radionuclides partition. In this presentation, initial results on interfacial reactivity between aluminate, boehmite, and gibbsite will be discussed. The impact of g and b radiation on boehmite and gibbsite will also be presented.

4:40pm **AC+AS+SA+SU-MoA10 Real Structure of Nanocrystalline Uranium based Hydrides Studied By the X-ray Scattering Methods**, ***Milan Dopita***, *L. Havela, L. Horak, M. Paukov,* Charles University, Prague, Czech Republic, *Z. Matej*, MAX-IV, Lund, Sweden

Interaction of hydrogen with uranium is not only an important issue for its nuclear and military applications but also contributes to understanding of the 5*f* magnetism. Uranium hydrides provide a unique tool to observe an impact of expansion of the U lattice, allowing formation of U moments and their ferromagnetic ordering. However, the electronic structure of uranium hydrides is not fully understood yet. Especially, the role of the real structure, i.e. the influence of the lattice defects, particle size in the nanocrystalline bulk materials and the preferred orientation of crystallites – the texture, the strains and stresses in the case of films is not well described, but can significantly influence electronic and magnetic properties of materials.

In our contribution we report the real structure of bulk and powder Mo- and Zr-alloyed uranium hydrides, prepared by rapid (splat) cooling and high pressure synthesis, and Mo alloyed uranium hydride films synthesized by reactive sputtering, using X-ray scattering methods. The sample series with different alloying element concentration as well as at different hydrogen pressure were prepared. Since the classical powder diffraction methods, as the profile analysis and/or Rietveld method, reach the limits of their applicability for the nanocrystalline uranium hydrides alloys in terms of the real structure description, the use of more advanced methods is necessary. Here we describe the total scattering method – pair distribution function analysis, and Debye equation calculation for simulations of the intensity scattered from nanocrystalline clusters.

The key results of our study were the determination of the phase composition and its evolution, as well as detailed atomic positions, which can influence the U-U spacings in individual phases, tuning the 5*f* magnetism. The methods are able to describe the particle size and defect distributions, the stress, strains, and textures in the films. In addition, the depth profiles and evolution of above mentioned parameters can be determined. Such X-ray analysis provides useful characterization of the sputter-deposited films, which are also used for fundamental electron spectroscopy studies of UH_3-based films, exhibiting much lower surface contamination by oxygen than comparable bulk material.

This work was supported by the project “Nanomaterials centre for advanced applications”, Project No. CZ.02.1.01/0.0/0.0/15_003/0000485, financed by ERDF.

Applied Surface Science Division
Room: 13 - Session AS+BI-MoA

Practical Surface Analysis: Complex, Organic and Bio-systems
Moderators: Scott Lea, Pacific Northwest National Laboratory, Paulina Rakowska, National Physical Laboratory, UK

2:00pm **AS+BI-MoA2 Environmental Charge Compensation - Near Ambient Pressure XPS as a Tool for Surface Chemical Analysis of Iinsulators without Charging Effects**, ***Paul Dietrich***, *A. Thissen,* SPECS Surface Nano Analysis GmbH, Germany, *S. Bahr*, Enviro Analytical Instruments GmbH, Germany

Since many decades XPS (or ESCA) is the well-accepted standard method for

non-destructive chemical analysis of solid surfaces. To fulfill this task existing ESCA tools

combine reliable quantitative chemical analysis with comfortable sample handling concepts,

integrated into fully automated compact designs.

Generically insulators will positively charge in XPS due to the irradiation with X-rays and

the emission of photoelectrons. Without compensation this effect leads to strong continuous

shifts and asymmetric line shapes of the emission lines in the spectra. To perform an exact

characterization and quantification of strongly insulating materials different concepts of

charge compensation or neutralization have been developed over the last decades. A short

overview is given starting from low energy electrons offered from so-called "flood guns" or

other sources, via compensation by a combination of electrons and ions to rare methods like

illumination with visible light during the analysis and compensation by the produced

electron-hole pairs. The opportunities and challenges of the different methods are compared.

The development of XPS method towards environmental or (near) ambient pressure

working conditions has revolutionized this method regarding applications. In-situ and

in-operando measurements in pressure of up to and above 25mbar are easily possible, even

with laboratory based systems and using EnviroESCA even in a standard analytical tool.

During the last months, measurements on insulators have shown, that they can be measured

with exception in surrounding pressures of a couple of mbar without any charging. This new

technique of charge neutralization is neamed Environmental Charge Compensation (ECC).

This presentation summarizes results of measurements on insulating polymer samples,

showing the resulting spectroscopic resolution for C1s and O1s emission lines. A

comparison for PET and PTFE to other neutralization techniques is given. In addition

measurements on bulk insulators from polymeric materials, ceramics, food samples,

aqueous solutions, stones, soil and even zeolites are shown, that cannot easily be obtained in

UHV based XPS systems.

Furthermore the effect is described in detail, including the influence of pressure and gas

composition on the charge neutralization. An outlook is presented towards completely new

resulting fields of application of XPS, when combined with ECC.

2:20pm **AS+BI-MoA3 Does Time Play a Role in Glyoxal and Hydrogen Peroxide Photochemical Aging?**, ***Fei Zhang****, X.F. Yu, X. Sui,* Pacific Northwest National Laboratory, *J.M. Chen,* Fudan University, *Z.H. Zhu, X.Y. Yu*, Pacific Northwest National Laboratory

Aqueous surfaces consisting of glyoxal and hydrogen peroxide (H_2O_2) after photochemical aging have been studied in a microfluidic reactor (System for Analysis at the Liquid Vacuum Interface, SALVI) by in situ liquid Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). Positive and negative ion mode mass spectra provide complementary information of the surface reactions. Compared with previous results using bulk solutions, our unique liquid surface molecular imaging approach makes it possible to observe glyoxal hydration (i.e., first and secondary products, hydrates), oxidation products (i.e., glyoxylic acid, oxalic acid, formic acid, malonic acid, tartaric acid), oligomers (i.e., $C_7H_{11}O_9^+$, $C_6H_5O_{10}^-$), water clusters (i.e., $(H_2O)_nH^+$, n< 43, $(H_2O)_nOH^-$, n< 44), and cluster ions (i.e.,$C_6H_{17}O_{12}^+$, $C_7H_9O_{11}^-$) with submicrometer spatial resolution. Spectral principal component analysis (PCA) is used to determine similarities and differences among photochemical aging samples ranging from 15 minutes to 8 hours. The oxidation products such as glyoxylic acid, glycolic acid, and tartaric acid tend to peak at around between 30 min and 1 h. UV aging; while oligomers and large water clusters (i.e., $(H_2O)_{22}OH^-$, $(H_2O)_{23}OH^-$,$(H_2O)_{24}OH^-$) form significantly at about 3 h. The oligomer formation reaches its maximum at 4 h., and reduces afterwards. Large water clusters (n> 15) become more significant as photochemical aging progresses, indicating more hydrophobicity at the aqueous surface as predicted by molecular dynamic simulation in earlier works. SIMS three-dimensional (3D) chemical mapping enables visualization of the surface mixing state at the molecular level. We have presented the temporal progression of the 3D surface mixing state of various products from glyoxal and hydrogen peroxide oxidation for the first time. Such physical measurements pave a new way to investigate complex surface reaction mechanisms as an important source of aqueous secondary organic aerosol (SOA) formation in atmospheric chemistry.

2:40pm **AS+BI-MoA4 Study of Drug Uptake and Action on Metabolic Processes at the Single-Cell Level using the 3D OrbiSIMS**, ***Ian S. Gilmore***, *M.K. Passarelli, M. Lorenz,* National Physical Laboratory, UK, *C.F. Newman, P.S. Marshall, A. West,* GlaxoSmithKline, UK, *P.D. Rakowska, R. Havelund, C.T. Dollery*, National Physical Laboratory, UK

A major quest for the pharmaceutical industry is the reduction of late-stage drug failure. Measurements that can identify future failure at the early stages of drug development are therefore of great importance. This requires label-free imaging of the distribution of pharmaceutical compounds and metabolites with subcellular resolution. We have previously shown [1] that ToF-SIMS can provide useful sub-cellular resolution images but analysis is limited by insufficient mass accuracy, mass resolving power for accurate identification of metabolites and sensitivity.

We have recently led the development of a powerful new hybrid instrument, the 3D OrbiSIMS [2], combining an Orbitrap^{TM}-based Thermo Scientific^{TM} Q Exactive^{TM} HF instrument and a dedicated ToF-SIMS 5. The instrument is equipped with high-resolution ion beams including a new micrometre resolution argon cluster ion beam for biomolecular imaging and 3D analysis of organics and an ultra-high resolution Bi cluster focussed ion beam with < 200 nm resolution.

In this study, we demonstrate the unparalleled ability for 2D and 3D metabolite imaging with sub-cellular resolution. We show significant variability of drug uptake at the single cell level and demonstrate direct evidence of up regulation of metabolites. This can only be revealed with a single-cell study. Furthermore, we demonstrate a new method for in situ matrix deposition for 3D imaging that significantly increases sensitivity. This is especially important for current drug candidates with Log P values ≤ 3 (Lipinski rule of five), which are known to have low molecular secondary ion yields. [3]

[1] M.K. Passarelli et al, Analytical chemistry 87 (13), 2015, 6696

[2] M.K. Passarelli et al, submitted, 2017

[3] J.L. Vorng et al, Analytical Chemistry 88 (22), 2016, 11028

3:00pm **AS+BI-MoA5 TOF-SIMS Cluster Beam Depth Profiling and 3D Imaging of Oral Drug Delivery Films**, ***Greg Gillen***, *S. Muramoto*, *J. Staymates*, *E. Robinson*, NIST

Dissolvable oral thin film (OTF) drug delivery systems are gaining increased interest as convenient alternatives to more conventional tablets and capsules for drug delivery applications. The OTF's are typically made by mixing an active pharmaceutical ingredient (API) into a dissolvable polymer that is administered to the patient by placing under the tongue or against the inside of the cheek. Direct adsorption of the API into the systemic circulation bypasses gastrointestinal delivery and can provide higher levels of bioavailability and a more rapid release profile in appropriate medications. One critical challenge with further development of OTF drug delivery systems is the lack of appropriate measurement tools for the characterization of API concentration, phase and dose uniformity throughout the depth of the polymer film (typically ~100 um in thickness). Furthermore, OTF's are currently manufactured as bulk sheets with fixed levels of API. This is a significant roadblock to realization of OTF's for personalized medicine where there is a growing interest in manufacturing of OTF's with individualized and patient-specific API dosages. One promising method of production of such films that is currently being explored in our laboratory is the used of drop on demand inkjet printing to precisely deposit individualized API doses onto prefabricated films.

In this work, we explore the utility of Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) using gaseous cluster ion beam (GCIB) depth profiling for the characterization of the lateral and in-depth distribution of API's in model OTF films. Three types of films were examined; (1) model thin films of pullulan, (2) model thin films of pullulan that had been dosed using drop on demand inkjet printing with various concentrations of relevant API's and (3), commercially available OTF films (single and multilayer films) containing the anti-opioid medications buprenorphine and naloxone which are widely used medications for treatment of opioid dependency. Cluster SIMS depth profiling was able to resolve compositional differences throughout the depth of each of these films (>70 um in thickness) and localize the individual API's. Furthermore, the ability to characterize the lateral and in depth distribution of API's in individual inkjet droplets will be demonstrated as well as the use of inkjet printing to prepare in situ concentration standards for evaluation of dosage variability. Finally, we also demonstrate the use THz Raman imaging for chemical identification of the API and possible phase changes due to the use of inkjet-printed formulations.

3:20pm **AS+BI-MoA6 Characterisation of Bioelectronic Material Surfaces using Surface Spectroscopies**, ***Sarah Coultas***, Kratos Analytical Limited, UK, *W. Boxford*, Kratos Analytical Ltd, UK, *C.J. Blomfield*, Kratos Analytical Limited, UK, *M. Firlak*, *J. Hardy*, Lancaster University, UK

Electromagnetic fields affect a variety of tissues (e.g. bone, muscle, nerve and skin) and play important roles in a multitude of biological processes. This has inspired the development of electrically conducting devices for biomedical applications, including: biosensors, drug delivery devices, cardiac/neural electrodes, and tissue scaffolds. It is noteworthy that there are a number of clinically approved devices capable of electrical stimulation of the body, all of which are designed for long term implantation. The first examples were developed in Sweden and include bionic eyes, ears and electrodes for deep brain stimulation (DBS). Recently there has been considerable industrial interest in the development and commercialisation of bioelectronic medicines. Bioelectronics is an emerging area of technology that promises broad impact in healthcare.

The detailed analysis of biomaterials and biomedical devices offers valuable insight into the underlying function of the products. The materials are composites of electroactive polymers (e.g. polypyrrole) and biopolymers (e.g. polysaccharides and proteins) that can be used for various applications (e.g. drug delivery, tissue scaffolds).

Here we demonstrate the application of surface spectroscopies, including XPS and UPS, to characterise bioelectronic materials in various morphologies (e.g. films and foams). We utilise a range of approaches to fully characterise the materials, including investigating any variations in composition either laterally or with depth. We also explore the usefulness of surface cleaning using Argon clusters.

References:

J. Rivnay, et al. Review on bioelectronics: Chem. Mater. 2014, 26, 679−685

G. G. Wallace, et al. Review on bioelectronics: Nanoscale. 2012, 4, 4327–4347

J. G. Hardy, et al. Article on bioelectronic drug delivery devices: J. Mater. Chem. B, 2014, 2(39), 6809-6822.

J. G. Hardy, et al. Article on instructive bioelectronic tissue scaffolds: Macromol. Biosci., 2015, 15, 1490-1496.

4:00pm **AS+BI-MoA8 High-resolution SIMS Imaging of Subcellular Structures**, ***Mary Kraft***, *A.N. Yeager*, University of Illinois at Urbana-Champaign, *P.K. Weber*, Lawrence Livermore National Laboratory **INVITED**

In mammalian cells, lipids and cholesterol form the selectively permeable plasma membrane that separates the cell from its surroundings, and the intracellular membranes that delineate the boundaries of organelles and transport vesicles. The distributions of cholesterol and each lipid species between these organelles is correlated with health and disease. The accumulation of cholesterol and certain lipid species within lysosomes and endosomes causes defects in intracellular trafficking that can be fatal if left untreated. The ability to image the relative abundances of cholesterol and distinct lipid species within intracellular compartments could lead to a better understanding of the biological mechanisms that regulate subcellular lipid distribution. For this purpose, we have combined metabolic stable isotope incorporation with secondary ion mass spectrometry (SIMS), which is performed on a Cameca NanoSIMS 50, to image the intracellular distributions of cholesterol and sphingolipids. By using depth profiling SIMS to image the distributions of ^{18}O-cholesterol and ^{15}N-sphingolipids within a portion of a Madin-Darby Canine Kidney (MDCK) cell, we determined that these two components are enriched within separate intracellular compartments. The sizes and relative positions of the ^{15}N- and ^{18}O- enriched intracellular features that are visible in the 3-D representations of the SIMS images suggest that the ^{15}N-sphingolipids are located within transport vesicles, whereas the ^{18}O-cholesterol seem to be concentrated within lipid droplets.

4:40pm **AS+BI-MoA10 EnviroESCA – Routine Surface Chemical Analysis under Environmental Conditions For Biological Samples**, ***Andreas Thissen***, *P. Dietrich*, SPECS Surface Nano Analysis GmbH, Germany, *S. Bahr*, Enviro Analytical Instruments GmbH, Germany, *M. Kjaervik*, *W. Unger*, Bundesanstalt für Materialforschung und -prüfung (BAM), Germany

Since many decades XPS (or ESCA) is the well-accepted standard method for

non-destructive chemical analysis of solid surfaces. To fulfill this task existing ESCA tools

combine reliable quantitative chemical analysis with comfortable sample handling concepts,

integrated into fully automated compact designs.

Over the last years it has been possible to develop XPS systems, that can work far beyond

the standard conditions of high or ultrahigh vacuum. Near Ambient Pressure (NAP) XPS has

become a fastly growing field in research inspiring many scientist to transfer the method to

completely new fields of application. Thus, by crossing the pressure gap, new insights in

complicated materials systems have become possible using either synchrotron radiation or

laboratory X-ray monochromators as excitation sources under NAP condtions.

Based on this experience SPECS Surface Nano Analysis GmbH has developed a revolutionary tool to realize the long existing dream in many analytical laboratories:

reproducible chemical surface analysis under any environmental condition. EnviroESCA

allows for different applications, like extremely fast solid surface analysis of degassing (but

also non-degassing) samples, ESCA analysis of liquids or liquid-solid interfaces, chemical

analysis of biological samples, materials and device analysis under working conditions.

After introduction of the technological realization a comprehensive survey of results will be

given starting from standard solid conductive samples under different pressure conditions,

bulk insulators with environmental charge compensation applied, high throughput analysis

of batches of similar objects, geological samples, chemical analysis of pharmaceuticals to

the comparative analysis of ultrapure liquid water with different aqueous solutions.

The application of Near Ambient Pressure XPS to biological specimen from plants and

animals, biofilms and bacteria, as well as food samples is a completely new field for

electron spectroscopic studies of the surface chemical composition.

An outlook is presented on the application to electrochemical and other in-operando devices.

Finally the influence of the ambient conditions on quantification in XPS will be

demonstrated and discussed.

This project has received funding from the EMPIR programme co-financed by the Participating

States and from the European Union’s Horizon 2020 research and innovation programme.

Spectroscopic Ellipsometry Focus Topic
Room: 9 - Session EL+AS+EM-MoA

Spectroscopic Ellipsometry: Novel Applications and Theoretical Approaches
Moderator: Maria Losurdo, CNR-NANOTEC

1:40pm **EL+AS+EM-MoA1 Temperature Dependent Mueller Matrix Measurements of Magnetised Ni near the Curie Temperature**, ***Farzin Abadizaman***, *S. Zollner*, New Mexico State University

The temperature dependence of the optical constants of the magnetized bulk Ni demonstrates an anomaly near the Curie temperature. We investigate this anomaly by taking a measurement of the temperature dependent Mueller Matrix (MM). Using spectroscopic ellipsometry at an energy 1.96 eV, the MM measurement was taken from 350 K to 500 K with 10 K steps, and from 500 K to 670 K with 1 K steps, and from 670 K to 730 K with 10 K steps.

In order to distinguish the anisotropic properties of the magnetized Ni from the windows effects, three samples (Ge, Ni, and SiO_2 on Si) were measured inside the cryostat in the energy range from 1 eV to 5 eV with 0.1 eV steps. The results show that the anisotropic elements of the MM behave in the same fashion for all samples, except for element M_{24},which depends on the sample.

The MM data of magnetized Ni indicate very small changes in the anisotropic portion of the MM compared to the windows effect. The authors believe that these changes are due to the magneto-optical Kerr effect. However, since a rotating-analyzer ellipsometer was used, the last row of the MM is absent and a complete MM measurement needs to be performed to find the magneto-optical Kerr effect in the other anisotropic elements too.

However, very large decreases in the isotropic MM elements were found near the Curie temperature. This means, the changes in optical constants near Tc are due to the on-diagonal Drude part of the dielectric tensor, which can be explained by s- to d-band electron-phonon scattering above and below T_c. These changes are absent when decreasing the temperature and for unmagnetized Ni.

2:00pm **EL+AS+EM-MoA2 Ellipsometry Based Observation of Material Ordering Process in Holography**, ***Hao Jiang***, *H. Peng*, *Y. Liao*, *S. Liu*, Huazhong University of Science and Technology, China

Ordered materials with superior performance have been constantly pursued. Nevertheless, the direct, precise and non-destructive observation of the ordering process, which is especially critical for continuous manufacturing, remains a formidable challenge. Herein, we introduce Mueller matrix ellipsometry (MME) as a nondestructive method to quantitatively observe the material ordering process during holography. This non-destructive observation directly offers the exact width, refractive index, nanoparticle weight fraction and volume fraction in each constructive (bright) or destructive (dark) interference area, which is impossible to be implemented using other existing techniques. Meanwhile, the width of dark region is observed to decrease while the width of bright region increases with an augmentation of the holographic recording time, distinct from previous assumption. More importantly, an apparent diffusion coefficient of 1.3×10^{-15} m^2 s^{-1} is determined on the basis of recording time-dependent grating structure observation, which is 3 orders of magnitude lower than the Stokes-Einstein prediction. The distinct diffusion coefficient is regarded to be the result of competition between the forth diffusion driven by the chemical reaction and backward diffusion arising from nanoparticle concentration gradient. This novel protocol is envisioned to pave the way for precisely and non-destructively understanding the ordered structure formation in electrics, photonics, photovoltaics, biomaterials and other disciplines.

2:20pm **EL+AS+EM-MoA3 Coherence in Polarimetry and Ellipsometry: Synthesizing Mueller Matrices in an Ellipsometer**, ***Oriol Arteaga***, Departament de Física Aplicada, Universitat de Barcelona, Spain **INVITED**

Interference phenomena are ubiquitous in optics and are the basis of the industry behind thin film optical coatings or thin film thickness measurements with ellipsometry. The interference of polarized beams was experimentally understood in 1819 when Arago and Fresnel derived the four laws governing the interference of polarized light. While spectroscopic ellipsometry provides information based on the position and number of interference oscillations in thin films, typically one has no macroscopic control of the beams that coherently superpose.

In this work we present a polarimetric analysis of an analogue of Young's double slit experiment that allows merging beams in a well-controlled manner. The experiment is analyzed with a new formalism that is useful to describe optical coherence and polarization and that shows that the superposition of two macroscopically distinguishable beams can be an effective method to experimentally synthesize Mueller matrices with on-demand polarization properties. This offers the opportunity of working with "synthesized" optical elements that behave just like "real" ones. We will discuss how this method can have a practical application in the construction of ellipsometers or polarimeters.

3:00pm **EL+AS+EM-MoA5 Femtosecond Spectroscopic Ellipsometry on Optoelectronic Materials and Photonic Structures**, ***Mateusz Rebarz***, *S.J. Espinoza,* ELI Beamlines - Czech Academy of Science, Czech Republic, *S. Richter, O. Herrfurth, R. Schmidt-Grund,* Universität Leipzig, Germany, *J. Andreasson,* Chalmers University of Technology, Sweden, *S. Zollner*, New Mexico State University

The ongoing progress in miniaturization and operational rates of electronic and optoelectronic devices obliges materials scientists to deeply understand the dynamics of the carriers upon external electromagnetic stimulus in very short time scale. Some phenomena such as scattering of electrons and phonons as well as recombination processes can be as short as tens of femtoseconds. All these processes affect the temporal and local dielectric constants and determine many operational parameters of the devices. In this work, we report on recent progress in developing a spectroscopic ellipsometer for characterization of ultrafast dynamic changes of dielectric properties in materials and photonic structures technologically relevant in optoelectronics. Our time-resolved ellipsometer is based on pump-probe technique and offers monitoring the time evolution of the dielectric properties in range 0-5 ns with time resolution ~100 fs in broadband spectral range (340-750 nm).

We present here the results of the measurements performed on Ge samples in comparison with theoretical predictions. Ultrafast phenomena such as excitation, relaxation and diffusion of charge carriers, band-gap renormalization and excitons screening will be discussed. In addition we report on the first data obtained from a ZnO-based planar microcavity especially on the temporal evolution of the microcavity modes. The time evolution of the ellipsometric parameters in the spectral range around the exciton-polariton mode will be discussed. We observed that such modes disappear upon the excitation, possibly due to screening of the excitons and re-appear after a few hundreds of femtoseconds as blueshifted modes. The investigation of the short-time dynamics of such modes can stimulate new theoretical approaches for the description of exciton-polariton systems.

3:20pm **EL+AS+EM-MoA6 Temperature Dependence of the Dielectric Function and Interband Critical Points of Bulk Germanium**, ***Carola Emminger***, *N. Samarasingha, F. Abadizaman, N.S. Fernando, S. Zollner*, New Mexico State University

Exploration of the optical properties of bulk germanium (Ge) is necessary for the advancement of Ge technology. In fact, many of the Ge applications depend on the dielectric function (ε), which is directly related to the electronic band structure. Here we investigate the effect of temperature on the optical properties and interband critical points (CPs), primarily the E_0 and $E_0+\Delta_0$ critical points of bulk Ge in the temperature range from 10 to 738 K using spectroscopic ellipsometry at 70° angle of incidence. The data was taken in two parts, in the near IR region and in the UV region, which provides data from 0.5 to 6.2 eV. The low temperature environment was created in a UHV cryostat with liquid helium and nitrogen as cryogens. To reduce the thickness of the native GeO_2 layer, the Ge sample was cleaned using ultra-pure water, isopropanol, an ultrasonic bath and ozone cleaning. It was possible to reduce the oxide thickness to about 11 Å at room temperature.

The authors used a two-phase model (GeO_2 layer/Ge substrate) and a parametric oscillator model with a set of adjustable parameters to extract the real and imaginary parts of the complex dielectric function of the bulk Ge for the whole temperature range. To investigate this temperature dependence of the CP parameters (threshold energy, broadening and phase angle) further, we also compared the second derivative $d^2\varepsilon/d^2\omega$ of the dielectric function with analytical line shapes.

The temperature has a significant influence on both the real and imaginary parts of the complex dielectric function of bulk Ge. This temperature dependent ε can be explained by a Bose-Einstein occupation factor. Due to the electron-phonon interaction, we find a temperature dependent red shift (shift to lower energies) of the E_0 and $E_0+\Delta_0$ critical point energies. The temperature independent spin orbit splitting Δ_0 is found to be 286 meV. A similar effect has been seen in the E_1, $E_1+\Delta_1$, E_0', and E_2 CP energies. These CPs are broadened and shifted to the lower energies with increasing temperature.

4:00pm **EL+AS+EM-MoA8 VUV Magneto-Optical Transient Ellipsometer**, ***Shirly Espinoza***, *J. Andreasson*, Institute of Physics ASCR, Czech Republic

This talk is about the ELIps instrument, an instrument that combines three advanced techniques of ellipsometry: VUV ellipsometry, Transient (Pump-probe) ellipsometry, and Magneto-optical ellipsometry [1].

The ELIps instrument allows users to work in a very wide range of energies from 1 eV to 40 eV. For measurements in the 1 eV to 6.5 eV range, it uses a transmission polarizer and analyzer combination. Meanwhile, for measurements in the 6.5–40 eV range, it uses a triple-reflection polarizer and analyzer combination. All the components are contained within a single UHV chamber designed with several additional ports to support future upgrades. For time resolved measurements in the VUV range the instrument will be used together with a high intensity High Harmonics Generation (HHG) source.

Time-resolved transient measurements of the optical properties of materials can be performed in the range of a few femtoseconds to nanoseconds. Initial experiments with transient absorption and transient ellipsometry in the NIR-UV range is being performed on proton-conducting materials for solid oxide fuel cell applications.

Additionally, ELIps is equipped with a Helmholtz coil, which allows the studies of the transverse magneto-optical Kerr effect on the sample, and with a cryostat for measurements at different temperatures.

Where is this instrument located? ELIps is in Prague, Czech Republic, at the European Extreme Light Infrastructure Beamlines (ELI Beamlines), a user facility project that will hold some of the most intense lasers in the world. It will open to the public on January 2018.

References

[1] S. Espinoza, G. Neuber, C. D. Brooks, B. Besner, M. Hashemi, M. Rübhausen and J. Andreasson. 2017. User oriented end-station on VUV pump-probe magneto-optical ellipsometry at ELI beamlines. *Applied Surface Science*. Published online. doi:10.1016/j.apsusc.2017.02.005

Acknowledgements

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4:20pm **EL+AS+EM-MoA9 Infrared Ellipsometric Spectroscopy of $Hg_{1-x}Cd_xTe$ Bulk Samples**, ***Yanqing Gao***, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, China

The infrared spectroscopic ellipsometry of $Hg_{1-x}Cd_xTe$ (x=0.195~0.37) bulk samples with different compositions were meaured. The refractive index n and extinction coefficient k were obtained. An obvious refractive index enhancement effect was observed in the refractive index spectra for each composition. The energy position of the maximal refractive index value equals approximately that of the band gap. With the decrease of the component, the refractive index increased and the peak position shifted to the low energy direction, which consistented with the absorption edge. The refractive index n at Eg changed linearly with the composition x.

4:40pm **EL+AS+EM-MoA10 Infrared Ellipsometry Study of the Photo-generated Charge Carriers at the (001) and (110) Surfaces of $SrTiO_3$ Crystals and the Interface of Corresponding $LaAlO_3/SrTiO_3$ Heterostructures**, ***Meghdad Yazdi-Rizi***, *P. Marsik, B. Mallett*, University of Fribourg, Switzerland, *K. Sen, A. Cerreta*, University of Fribourg, *A. Dubroka*, Masaryk University, *M. Scigaj, F. Sánchez, G. Herranz*, Institut de Ciència de Materials de Barcelona, *C. Bernhard*, University of Fribourg, Switzerland

With infrared (IR) ellipsometry and DC resistance measurements we investigated the photo-doping at the (001) and (110) surfaces of $SrTiO_3$ (STO) single crystals and at the corresponding interfaces of $LaAlO_3/SrTiO_3$ (LAO/STO) heterostructures. In the bare STO crystals we find that the photo-generated charge carriers, which accumulate near the (001) surface, have a similar depth profile and sheet carrier concentration as the confined electrons that were previously observed in LAO/STO (001) heterostructures. A large fraction of these photo-generated charge carriers persist at low temperature at the STO (001) surface even after the UV light has been switched off again. These persistent charge carriers seem to originate from oxygen vacancies that are trapped at the structural domain boundaries which develop below the so-called antiferrodistortive transition at T^* = 105 K. This is most evident from a corresponding photo-doping study of the DC transport in STO (110) crystals for which the concentration of these domain boundaries can be modified by applying a weak uniaxial stress. The oxygen vacancies and their trapping by defects are also the source of the electrons that are confined to the interface of LAO/STO (110) heterostructures which likely do not have a polar discontinuity as in LAO/STO (001). In the former, the trapping and clustering of the oxygen vacancies also has a strong influence on the anisotropy of the charge carrier mobility. We show that this anisotropy can be readily varied and even inverted by various means, such as a gentle thermal treatment, UV irradiation, or even a weak uniaxial stress. Our experiments suggest that extended defects, which develop over long time periods (of weeks to months), can strongly influence the response of the confined charge carriers at the LAO/STO (110) interface.

Plasma Science and Technology Division
Room: 23 - Session PS+AS+SS-MoA

Plasma Surface Interactions

Moderators: Michael Gordon, University of California at Santa Barbara, Ying Zhang, Applied Materials, Inc.

1:40pm **PS+AS+SS-MoA1 Exploring the Gas-Surface Interface in NxOy Plasma Surface Modification of Zeolite Materials for Environmental Applications**, ***Angela Hanna****, *E.R. Fisher*, Colorado State University

With increasing concern for environmental health and climate change, there is a greater need to explore fundamental reactivity of pollutant species. Improving the effectiveness of substrates used in vehicular emissions abatement hinges on the ability to discern the contributions of gas-phase species in surface reactions. Here, inductively-coupled N_xO_y plasma systems were investigated to determine relationships between precursor chemistry and gas-surface interface interactions with different substrates. Precursor chemistry was probed via gas-phase diagnostics; time-resolved optical emission data elucidated NO (g) and N_2 (g) production kinetics from N_xO_y source gases, whereas steady-state emission and absorbance data provide information on energy partitioning between different degrees of freedom (e.g. vibrational and rotational modes). Specifically, we have determined rotational (T_R) and vibrational (T_V) temperatures for N_2 ($B^3\Pi_g \leftrightarrow C^3\Pi_u$) and NO ($X^2\Pi \leftrightarrow A^2\ \Sigma^+$). T_R and T_V for both molecules show strong positive correlations with applied rf power, as well as a negative correlation with system pressure. T_V is significantly higher than T_R for both N_2 and NO,

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* **Coburn & Winters Student Award Finalist**

regardless of precursor, with T_V ranging from ~2000 K to >3000K and T_R having values between ~300 K and 1000 K. Ultimately, these data afford significant insight into increased understanding of molecule formation and decomposition pathways, as well as overall plasma chemistry in nitrogen and oxygen-containing plasma systems of interest to pollution abatement. Similarly, interface studies explored the influence of both non-catalytic (e.g. Si wafers) and catalytic (e.g. zeolites, Pt wire) substrates on the gas-phase chemistry in the same plasma systems. X-ray photoelectron spectroscopy and scanning electron microscopy analyses of surface oxidation and morphological changes resulting from plasma processing will be presented. Furthermore, we will describe plasma surface modification of zeolites, in both a static plasma reactor and a rotating drum reactor. Our holistic approach to employing diagnostics tools to characterize the plasma, the surface, and the gas-surface interface suggests a more thorough evaluation of plasma processing for N_xO_y emission control.

2:00pm **PS+AS+SS-MoA2 Effects of Ion induced Damages on Etching Characteristics of ITO Thin Films**

Hu Li, *K. Karahashi*, Osaka University, Japan, *M. Fukasawa, A. Hirata, K. Nagahata, T. Tatsumi*, Sony Semiconductor Solutions Corporation, Japan, *S. Hamaguchi*, Osaka University, Japan

Micro-fabrication of transparent conducing oxides (TCOs), such as tin-doped indium oxide (ITO) and zinc oxide (ZnO), has been performed for optoelectronic devices such as solar panels and head-mounted liquid crystal displays. With the increasing demand of such devices, more efficient and more controllable fabrication technologies for patterning of TCOs are highly required. Reactive ion etching (RIE), which uses energetic reactive ions and typically allows high etch rates and high selectivity over hard masks, may be suitable for high-resolution pattering of TCOs. Hydrocarbon-based non-corrosive gases such as CH_4 and methanol have been used for RIE processes of TCOs. However, etching reactions and mechanisms of such processes have not been well understood. Therefore, the goal of this study is to clarify the mechanisms of RIE of TCOs by hydrocarbon-based plasmas.

In this study, sputtering yields of ITO were measured with the use of a mass-selected ion beam system, which allows the injection of only desired ion species with a specified incident energy into a substrate set in an ultra-high vacuum chamber. It has been found that the physical sputtering yield of an ITO film increases with pre-injection of energetic hydrogen (H) or helium (He) ions, which indicates that some atoms of the modified ITO film are less tightly bound and become more amenable to physical sputtering. The X-ray Photoelectron Spectroscopy (XPS) observation of ITO films pre-treated by energetic H or He ion injections has shown that the increase of the sputtering yield cannot be explained by the surface reduction of ITO films. In our preliminary study on ZnO, we have observed by Transmission Electron Microscopy (TEM) that the grain sizes of a ZnO film decrease after the film is exposed to energetic He ion injection. Therefore we surmise that grain sizes of ITO also similarly decrease and consequently the regions of grain boundaries increase after the film is pretreated by energetic H or He ions. By definition, atoms at grain boundaries are less tightly bonded with surrounding atoms than those in the crystalline bulk and therefore the increase of the grain boundaries is likely to contribute to the increase of the sputtering yield of the film.

2:20pm **PS+AS+SS-MoA3 Nitriding Process for Next-generation Semiconductor Devices by VHF (162 MHz) Plasma Source**

YouJin Ji, *K.S. Kim, K.H. Kim, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

Recently, for low power and high performance of semiconductor devices, the gate oxide thickness is scaled down and gate line-width is reduced. As a result, the role of nitride layer on gate oxide has become crucial to prevent the penetration of boron through thin gate oxide. In addition, high step coverage characteristics that are applicable to fine line patterns in a semiconductor device are also demanded. To keep pace with these detailed requirements, nitriding processes of the deposited silicon oxide employing conventional 13.56 MHz plasma source and N_2 as the nitriding gas has been generally utilized. However, 13.56 MHz plasma is difficult to decompose N_2 gas sufficiently, therefore, the thickness and nitrogen percentage of the oxynitride layer obtained by nitriding process are limited. In addition, high temperature operation above 200 °C can also cause the degradation of the device. In this study, a VHF (162 MHz) multi-tile plasma source was used for the decomposition of N_2 gas and the effect of the plasma conditions of VHF multi-tile plasma source on the nitridation of silicon oxide at room temperature was investigated. Using the VHF (162 MHz) plasmas, high density nitrogen plasmas with a low electron temperature and high vibration temperature were generated and, with these plasmas, dense oxynitride films with high nitrogen contents could be fabricated. Also, by controlling the plasma conditions, highly uniform oxynitride films with a high step coverage could be also obtained.

2:40pm **PS+AS+SS-MoA4 Defect Generation in Graphene Films by Low-Pressure Inductively Coupled Argon Plasmas Treatments**

X. Glad, P. Vinchon, S. Boivin, G. Robert-Bigras, ***Luc Stafford***, Université de Montréal, Canada

For many applications, graphene properties need to be tuned by post-processing techniques, such as plasma treatment. The latter is commonly used as a graphene doping method [1]. However, the decoupling of doping and damage mechanisms may be complex. Typically, damage studies on graphene are carried out using high-energy electron beams [2] or ion beams at energy above a few tens of eV [3]. Nonetheless, a few studies showed that plasma treatment may induce damage on graphite although incident ions transfer less energy to the graphite lattice than the energy threshold displacement (T_d = 15-20 eV) [4]. The literature is strongly lacking systematic and parametric experimental studies of the defects induced in graphene by non-reactive plasma with low-energy ions.

The aim of this study is to investigate the defect formation on graphene films by low-pressure argon inductively coupled plasmas in the very low ion energy range (< 15 eV). To do so, plasma parameters have been assessed by Langmuir probe (LP) and mass spectrometry to determine conditions of fixed ion fluence but different ion energy. Such conditions were obtained by increasing the pressure while lowering the applied rf power and adjusting the treatment time. Raman spectroscopy (RS) was then carried out on each treated graphene sample to evaluate and identify the damage generation.

Our results reveal two contributions on the defect generation: one proportional with the ion energy, the other with the gas pressure. LP and optical absorption measurements have been coupled with a collisional-radiative model to estimate the main energetic species power fluxes (ions, VUV photons, resonant and metastable states). It showed that the ion contribution is the dominant one for each condition. Thus, it seems that with lower ion energy and higher pressure, surface diffusion and redeposition processes become preponderant resulting in a higher density of amorphous carbon found on the graphene sheet, as evidenced by RS. The occurrence of this amorphous matter would explain the high intensity D/G band ratio observed, even at very low-ion energy. Preliminary results thus suggest that, to achieve graphene doping by mild plasma treatment, lower pressure is desirable since minimal production of amorphous carbon is observed.

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3:00pm **PS+AS+SS-MoA5 The Role of Plasma Species and Sample Composition on Dense Amorphous Carbon Layer Formation and Polymer Etching Behavior**

Adam Pranda, *S.A. Gutierrez-Razo, Z. Tomova, J.T. Fourkas, G.S. Oehrlein*, University of Maryland, College Park

Numerous polymer etching models have been previously developed to correlate the structure or composition of the polymer to the plasma etching behavior[1]. A key assumption in these models is that the polymer structure remains homogenous as it is etched. For applications in photoresist pattern transfer, this assumption is not valid since high-energy ion bombardment results in the formation of a heterogeneous structure consisting of a 2-3 nanometer thick dense amorphous carbon (DAC) layer on the polymer surface which mediates the overall etch rate.

In this work, we experimentally examined several key plasma and sample parameters that impact the etching behavior for a set of model polymers and PR193 and PR248-type photoresist. These parameters include plasma composition, fluxes of incident species in the plasma, intensity of ion bombardment-induced surface modifications that affect the etching behavior, polymer chemical composition and molecular structure, along with UV and VUV sensitivity in a plasma environment. From our experimental work, we have found that the thickness and intensity of the DAC layer is highly dependent on the chosen plasma parameters and the polymer composition/molecular structure.

We compare various models of the etching behavior of a polymer based on parameters such as the polymer chemical composition/structure and the flux of incident species in the plasma relative to experimentally observed relationships. Of key significance is the relationship between reactive plasma species and the state of the DAC layer.

One of the experimental correlations we have identified is that a molecular structure consisting of a greater ratio of carbon carbon-type bonding results in a more optically dense DAC layer, which limits the ion flux that reaches the bulk layer, and thus leads to a lower steady-state etch rate. In the presence of any reactive species in the plasma, such as oxygen or fluorocarbon, there is an additional component to the etch rate due to chemical sputtering which results in an increase in the etch yield of the DAC layer. Once the DAC layer is sufficiently depleted, the ion flux reaching the bulk layer increases and thus the bulk etch rate increases as well. Utilizing the experimental results, we seek to arrive at an etching model that can be applied in the development of new photoresists that attain a target steady-state etch rate.

The authors gratefully acknowledge the financial support of this work by the National Science Foundation (NSF CMMI-1449309) and the US Department of Energy Office of Fusion Energy Sciences (DE-SC0001939).

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3:20pm **PS+AS+SS-MoA6 Control of Ion Energy Distributions on Insulating Surfaces**, ***Tyler List***, *T. Ma, V.M. Donnelly, D.J. Economou*, University of Houston

A method for controlling ion energies on insulating substrates using pulsed plasma is presented. A synchronous bias voltage was applied to a boundary electrode in the afterglow of a pulsed plasma, resulting in a positive ion flux to the insulating substrate. To avoid excessive charging of the surface, DC square pulses were periodically applied to the chuck holding the substrate, to attract an electron swarm to the surface and neutralize the surface charge. Surface potential measurements were used to validate the proposed scheme. The effect of pulse width, amplitude, and frequency on the resulting surface potential waveform was examined. A Retarding Field Energy Analyzer was used to measure the ion energy distribution. When corrected for the non-uniform charge distribution prevailing when the applied RF frequency is less than the ion sheath transit frequency, the IED was similar to that predicted by a mathematical model of the system. Etching of quartz discs and 1000 nm-thick SiO_2 films, thermally grown on Si wafers, was also performed. For both types of substrates, beyond an etching threshold, the etching rate increased linearly with the square root of chuck bias. No clear effect of the boundary electrode bias voltage on the etching rate was observed. The behavior of etching rate as a function of the (DC chuck bias) pulse width mirrored the dependence of surface potential on pulse width. Work supported by NSF and DOE.

4:00pm **PS+AS+SS-MoA8 Ultra-high Si_3N_4 to SiO_2 Selective Etching by Fluorocarbon Based Remote Plasma**, ***Chen Li***, University of Maryland, College Park, *T. Hofmann, K. Edinger*, Carl Zeiss SMT GmbH, *G.S. Oehrlein*, University of Maryland, College Park

Plasma etching processes capable of highly selective Si_3N_4 to SiO_2 removal are increasingly required in fabrication of current integrated circuit devices. We report fluorocarbon (FC) based remote plasma etching processes for Si_3N_4 and SiO_2 substrates using inductively coupled plasma (ICP) and electron cyclotron wave resonance (ECWR) plasma reactors. For the remote plasma operating conditions direct ion bombardment of the sample surface is prevented and etching is primarily due to chemical reactions by neutral radicals. Such conditions can be realized by either high processing pressure for a remote ICP source or a neutralization plate for an ECWR source. Combinations of fluorocarbon gases, e.g. CF_4, with O_2 and N_2 additives have been evaluated. Etching behavior and surface properties are monitored using *in situ* ellipsometry. Optical emission spectroscopy (OES) has been used to evaluate the plasma gas phase chemistry. We show that ultra-high Si_3N_4 to SiO_2 etching selectivity can be achieved under remote plasma conditions in both reactors, and that control of the feed gas chemistry plays a key role. As is well-known, low levels of O_2 increase oxidation of FC gases and atomic F generation, which leads to increasing Si_3N_4 etch rate, whereas for high O_2 levels the F concentration is reduced and surface oxidation takes place. For these F-rich remote plasma conditions, SiO_2 is hardly etched and Si_3N_4 to SiO_2 etching selectivity of 7 and 87 were observed for the ICP and ECWR system, respectively. The observed etching behavior will be discussed using surface chemical studies of Si_3N_4 and SiO_2 by vacuum transferred x-ray photoelectron spectroscopy (XPS).

4:20pm **PS+AS+SS-MoA9 Effect of Temporal Variation of Discharge on Photon-induced Interface Defects in Pulse-modulated Inductively Coupled Plasma**, ***Yasufumi Miyoshi***, *M. Fukasawa, K. Nagahata*, Sony Semiconductor Solutions Corporation, Japan, *K. Ishikawa, M. Sekine, M. Hori*, Nagoya University, Japan, *T. Tatsumi*, Sony Semiconductor Solutions Corporation, Japan

It is important to reduce photon-induced interface defects, which degrade the performance of electric devices. Ishikawa et al. reported that using pulse-time-modulated plasma reduces UV photon-induced defects [1]. In this study, we investigated how temporal variation of the discharge affected these defects in pulse-modulated $Ar/CF_4/O_2$ inductively coupled plasma (ICP).

In this study, we varied the ICP source pulse frequency (0.5–20 kHz) and duty ratio (50–100%) as well as the gas ratio of Ar/CF_4. To investigate the UV radiation damage, the interface-trap density (D_{it}) was measured by using on-wafer pallet for plasma evaluation (PAPE) [2]. We used D_{it}, which is proportional to the UV fluence from discharge, as an indicator of UV damage. Temporal changes in the optical emission spectroscopy (OES) intensity of pulsed plasma were also investigated.

The measured D_{it} was lower than that in the CW at lower frequencies but was higher at higher frequencies (> 10 KHz). Increasing the frequency increased D_{it}, which reached a maximum at 10 kHz for $Ar/CF_4 = 1$, and then decreased D_{it}. Using a lower CF_4 ratio shifted the maximum D_{it} to a lower frequency.

This frequency-dependent behavior comes from the transient behavior of the pulsed ICP. Time-resolved OES revealed an optical emission overshoot after ignition caused by the variation in the electron temperature and number density in the early ON phase. The number of overshoots increased with increasing frequency, increasing the UV fluence and D_{it}. At higher frequencies, the variation in the electron temperature and number density were suppressed due to stepwise ionization from residual long-lived metastable species in the early ON phase [3]. This behavior considerably decreased overshoot amplitude, in turn decreasing the UV fluence and D_{it}. At the lower CF_4 ratio, quenching of the metastable species by CF_4 decreased and the lifetime of the metastable species during the OFF phase likely increased. Therefore, we presume that, at the lower CF_4 ratio, the overshoot amplitude began to decrease at a lower frequency than when $Ar/CF_4 = 1$ and the maximum D_{it} consequently shifted to a lower frequency.

These results show that controlling the temporal variation of a pulse-modulated plasma is essential to reduce the photon-induced damage it causes during plasma processes.

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4:40pm **PS+AS+SS-MoA10 Surface Mechanisms on Dielectric Surfaces Exposed to Low Pressure Glow Discharge and Atmospheric Pressure Plasma Jets**, ***Olivier Guaitella***, *A.S. Morillo-Candas*, Ecole Polytechnique - CNRS, France, *A. Sobota*, Eindhoven University of Technology, The Netherlands, *E. Slikboer, D. Marinov*, Ecole Polytechnique - CNRS, France, *B. Klarenaar, R. Engeln*, Eindhoven University of Technology, The Netherlands, *V. Guerra*, Instituto Superior Tecnico, Lisbon, Portugal **INVITED**

New applications of Non Thermal Plasmas (NTP) at atmospheric pressure such as biomedical applications, air treatment or CO2 recycling are growing rapidly with the better control of these plasma sources. All these applications rely on the effect of a transient plasma discharge with complex surfaces such as porous catalyst or biological tissues for instance. The interaction of plasma with surfaces is always a very challenging topic because of the multiplicity of phenomena modifying the surface but also because of the reverse influence of the substrate on the plasma properties. Therefore most of the studies dedicated to plasma surface interactions are performed with very low pressure plasmas and ideal model surfaces. No conclusion can be drawn on surface mechanisms if the plasma in contact with the surface is not well characterized while being in contact with the surface of interest.

The originality of the approach we have developed consists in the utilization a low pressure (1-10 mbar) pulsed dc discharge for investigation of elementary processes on the surface of real catalytic materials that are also studied in atmospheric pressure DBDs.

The pulsed glow discharge allow us to measure the dynamic of plasma parameters (Electric field, Gas temperature, radical densities, vibrational excitation etc…) to give constraints to kinetics models allowing us to distinguish between gas phase reactions and the role of elementary surface processes such as O atoms recombination or molecule conversion on surface. Various diagnostics have been used in the gas phase including Doppler broadened TALIF (for O atoms density and gas temperature), or step scan FTIR (for vibrational temperature of CO_2 and CO). Infrared absorption is performed in transmission directly through catalyst pellets exposed to the same plasma to investigate adsorbed molecules.

In parallel, other diagnostics are being developed to obtain electric field, temperature profile and adsorbed species on surfaces exposed to atmospheric pressure plasma sources. A kHz plasma jet configuration is used for its reproducibility as a first model plasma source for studying ionization wave interaction with surfaces. Surface electric field, charge deposited and is obtained under controlled atmosphere from polarization technique based on Pockels effect. Infrared absorption in transmission through catalyst samples is also used under plasma jet exposure.

The use of reproducible plasma sources allowing the combination of gas phase diagnostics and in situ surface diagnostics gives a new perspective on the importance of surface processes even at elevated pressures.

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

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

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

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

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

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

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

This research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.

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

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

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

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

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

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

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

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

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

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

References

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4:40pm **SP+2D+AS+NS+SS-MoA10 The Difference between Electron and Hole Dopant of Magnetic Element to the Superconductivity in $BaFe_2As_2$**, ***Qiang Zou***, *L. Li, A. Sefat, D.S. Parker, Z. Gai*, Oak Ridge National Laboratory

The effect of magnetism and spin excitation in the Fe-based superconductors (FeSC) is crucial to understand their superconductivity. Both electron-(Ni) and hole-(Cr) dopant of magnetic elements could lead to suppression of the magnetic/structural phase transition in $BaFe_2As_2$. However, the Cr doped $BaFe_2As_2$ doesn't show the superconductivity. Using scanning tunneling microscopy/spectroscopy, here, we compared the electronic properties of $BaFe_2$-xNixAs$_2$ and $BaFe_2$-xCrxAs$_2$ at various temperatures. Our results will shed the light on the microscopic understanding of relation between the superconductivity and magnetism in the FeSC. This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

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

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

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

Surface Science Division
Room: 25 - Session SS+AS+HC-MoA

Surface Science for Energy and the Environment
Moderators: Steven Bernasek, Yale-National University of Singapore, Bruce Koel, Princeton University

2:20pm **SS+AS+HC-MoA3 Photochemistry of CO, Acetone and O_2 on Reduced Rutile $TiO_2(110)$**, ***Greg Kimmel***, *N.G. Petrik, M.A. Henderson*, Pacific Northwest National Laboratory **INVITED**

TiO_2 is an important photocatalyst with many practical applications. However, a fundamental understanding of the thermal and non-thermal reactions on TiO_2 surfaces is still lacking. We use ultrahigh vacuum (UHV) surface science techniques to investigate in detail representative reactions on single crystal rutile $TiO_2(110)$. For this talk, I will focus on the ultraviolet (UV) photon-stimulated reactions of CO, acetone and oxygen adsorbed on $TiO_2(110)$. For CO co-adsorbed with O_2, CO_2 is produced during UV irradiation. The CO_2 preferentially desorbs in the plane perpendicular to the bridge-bonded oxygen (BBO) rows at an angle of 45°. Furthermore, the production rate of CO_2 is zero when the UV irradiation starts and reaches a maximum value at intermediate times before decaying at longer times. The results demonstrate that the photooxidation of CO is a multi-step reaction that proceeds through a metastable intermediate state that is oriented perpendicular to the BBO rows. This state is consistent with an O-O-C-O state found via density functional theory. For acetone co-adsorbed with oxygen, previous research suggests that a thermal reaction between acetone and adsorbed oxygen to form an acetone diolate precedes the photochemistry. During UV irradiation, a methyl radical is ejected leaving acetate on the surface. Using infrared reflection absorption spectroscopy (IRAS), we have identified the acetone diolate. We have also measured the angular distribution of the photodesorbing methyl radicals. Consistent with its ejection from acetone diolate, we observe a peak in the distribution at ~45° in the plane perpendicular to the BBO rows. However, a second photodesorption peak normal to the surface indicates that a second, previously unidentified, reaction channel is available. We attribute this second channel to the photo-induced formation of an enolate intermediate. When only O_2 is adsorbed on $TiO_2(110)$, its photochemistry depends on the coverage. For small coverages, only ~14% desorbs while the rest either dissociates during UV irradiation, or remains molecularly adsorbed on the surface. For the maximum coverage of chemisorbed oxygen, the fraction of O_2 that photodesorbs is ~45%. While photo-generated holes are responsible for the O_2 photodesorption, photo-generated electrons are responsible for the photo-induced O_2 dissociation. In general, these studies provide new insights into mechanisms responsible for the photochemistry of small molecules on TiO_2.

3:00pm **SS+AS+HC-MoA5 The Role of Band Alignment in Ketone Photooxidation on $TiO_2(110)$**, ***Amanda Muraca***, Stony Brook University, *M.G. White*, Brookhaven National Lab and Stony Brook University

Organic photooxidation processes on the $TiO_2(110)$ surface often show enhanced photoproduct yields in the presence of oxygen. For a series of simple ketones, it has widely been established that the photoactive surface species is a ketone-oxygen complex (η_2-ketone diolate) formed by interaction with O-adatoms, whereas the η_1-bound ketone is mostly photo-inactive.[1] The question remains, however, why the ketone-oxygen complexes are more photoactive than the adsorbed ketone alone. One possible explanation is that the diolate species have higher densities of molecular states near the valence band maximum (VBM) of $TiO_{2,}$ where resonant electron transfer to thermalized holes is expected to occur. To test this hypothesis, a series of methyl photoyield measurements, with and without co-adsorbed oxygen, were compared for a number of substituted ketone molecules ($R(CH_3)CO$; R = H, methyl, ethyl, butyl, propyl, phenyl, and trifluoromethyl) with varying ionization potentials (IPs). Experimentally, we observe a near linear correlation between the methyl photoproduct enhancement yields (diolate vs ketone) and the IPs of the bare ketone. These results suggest that as the ketone IP moves to higher energies, its hybridized orbitals move further (deeper) from the VBM and thereby exhibit a larger photoproduct enhancement when forming the ketone-diolate. This explanation points to orbital band alignment as the key factor determining ketone photoxidation activity, but this conclusion is largely based on the gas-phase properties and well established ideas of substituent effects. To gain more insight on our experimental results, we are currently using electronic structure calculations, both cluster models and periodic DFT, that could potentially provide more detail on band alignments for these molecules bound on the $TiO_2(110)$ surface.

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3:20pm **SS+AS+HC-MoA6 Storing Gases in Nanoporous Metal organic Frameworks Materials with a Surface Barrier Layer**, ***Kui Tan***, the University of Texas at Dallas, *S. Jensen, S. Zuluaga*, Wake Forest University, *E. Fuentes, E. Mattson, J.-F. Veyan*, University of Texas at Dallas, *H. Wang, J. Li*, Rutgers University, *T. Thonhauser*, Wake Forest University, *Y.J. Chabal*, University of Texas at Dallas

Enhancing gas adsorption in porous materials such as metal organic frameworks (MOFs) is critical to many technologies such as energy storage and gas capture and separation**.** In contrast to the previous efforts focusing on chemically modifying the entire MOFs structure to increase the affinity to gas molecules, in our recent work [Nature Communications, 2016, 7, 13871], we demonstrated an entirely new approach to trap small molecules by depositing a layer of ethylenediamine (EDA) on the external surface without penetrating inside the bulk of crystals in the gas loading process, and forms a monolayer cap that can effectively trap weakly adsorbed molecules (CO, CO_2, SO_2, C_2H_4, NO) or prevent their penetration. A combination of surface sensitive techniques *in-situ* infrared spectroscopy, X-ray photoelectron spectroscopy with gas cluster sputtering, low energy ion spectroscopy, and *ab initio* calculations demonstrate that the EDA layer is less than 1nm thick and arranges in a manner that increases CO diffusion barrier by ~24 times. Motivated by this finding, we further explore other capping media to store molecules inside MOFs. The latest experimental results suggest at least two ways: one is the deposition of a thin layer of aluminum oxide exclusively onto the external surface of certain MOFs with a narrower pore size (< 1.2 nm) by using common atomic layer disposition (ALD) precursor trimethylaluminum (TMA). Aluminum oxide is not able to grow inside MOFs since the reactivity of TMA with adsorbed H_2O is significantly reduced due to nano-confinement effects; another convenient way is post-exposure of gas-loaded MOF-74 to NH_3. NH_3 is preferentially adsorbed on the outer layer of MOFs crystals during the controlled exposure time (<10 min), as a result of which, the diffusion barrier of small gas molecules such as CO, CO_2, SO_2 in NH_3 decorated MOFs channels dramatically increases by the hydrogen bonding interaction. The ability to create surface barrier layers on MOFs external surfaces constitutes a new paradigm for trapping small gas molecules within nanoporous materials in general, and in MOFs in particular.

4:00pm **SS+AS+HC-MoA8 Active Species and Structures of Modified Oxide Catalysts for the Oxygen Evolution Reaction (OER)**, *Z. Chen,* Princeton University, *L. Cai,* Xi'an Jiaotong University, China, ***Bruce Koel***, Princeton University

Transition metal oxides (TMOs) are promising catalysts for oxygen evolution with the potential to replace precious metal-based catalysts (e.g. IrO_x and RuO_x). Significant improvements to the OER activity of TMOs have been made by tailoring the morphology and crystal structure of the catalysts, incorporating dopants, as well as using conductive supports. However, clear structure-activity correlations remain elusive because of the complex composition and structure of TMO catalysts. In this contribution, we utilizing a range of spectroscopic techniques for characterization of Ce-modified copper oxide (CuO_x) and Ni-modified cobalt (oxy)hydroxides to reveal the OER active species and structures of these catalysts. In the case of Ce-modified CuO_x, Ce incorporation (6.9 at%) into CuO_x led to 3.3 times greater OER activity compared to pure CuO_x and this is coincident with significant structural changes due to an increasing amount of disorder. By combining X-ray photoelectron and Raman spectroscopy techniques, a strong correlation between OER performance with tetravalent Ce (Ce^{4+}) ions was observed up to a concentration corresponding to CeO_2 phase segregation. We propose a strong promoting effect of Ce^{4+} for OER in this system. In the case of Ni-modified CoO_xH_y, operando Raman spectroscopy was used to reveal a drastic transformation of a spinel Co_3O_4-like structure into a more active (oxy)hydroxide structure under applied potential. Such a transformation was only observed in the presence of uniformly distributed Ni ions. These two examples, i.e. the promoting effect of Ce^{4+} and the formation of active OER structures in Ni-modified CoO_xH_y, reveal the importance of chemical state and local structure considerations for the rational design of OER oxide-based OER catalysts.

4:40pm **SS+AS+HC-MoA10 Cactus Based-Mucilage as an Alternative Natural Dispersant for Oil Spill Applications**, ***Fei Guo***, *D. Steebins, S. Thomas, R. Toomey, N. Alcantar*, University of South Florida

Functional surfactants from natural materials have the advantage of being biodegradable and can be obtained through sustainable agriculture. The functional natural surfactants was extracted from the *Opuntia ficus indica* cactus plant. The properties of the cactus plant-based mucilage were studied on the surface tension change, droplet size, and stability of Oil in Water (O/W) emulsions, toxicity, and dispersion effectiveness. Surface tension test was used to quantify the variation of surface tension of the Oil/Water (O/W) emulsion with the application of cactus mucilage and conventional dispersants (COREXIT 9500). The factors and the levels of each factor were as follows: DOR (mg/mg) (control, 1:200, 1:100, 1:50, and 1:20), Volume ratio of oil (3 and 6% v/v). It is observed that the application of NE reduced the surface tensions of the O/W emulsions. It also can be seen that the surface tensions of the O/W emulsion displayed a distinction among the different DORs at a lower volume ratio of oil. The results of the dispersion obtained using mucilage extracts were compared with using COREXIT 9500. The surface tensions of emulsions with cactus mucilage were similar as that with COREXIT 9500. The average droplet size in the systems with cactus mucilage were smaller when compared with the systems using the COREXIT 9500. Smaller droplet size implies higher emulsion stability, and may improve the biodegradation of oil. The baffled flask test was conducted to determine the influence of three environmental factors with cactus mucilage on oil dispersion. The percentage effectiveness of the dispersion was the response variable for this experiment. The factors and the levels of each factor were as follows: DOR (mg/mg) (control, 1:200, 1:100, 1:75, 1:50, 1:35, and 1:20), salinity of the synthetic seawater (10 and 35 PSU), and mixing speed (150, 200, and 250 rpm). The results showed that the dispersion effectiveness increased as DOR increased. There was also a good distinction among the different DORs. The increasing of the amount of cactus mucilage caused a reduction of the interfacial tension of O/W emulsion which made it easier to form the oil droplets. The cactus mucilage performed better at a lower salinity. The toxicity of the mucilage and COREXIT 9500 were evaluated by a standard EPA toxicity test using Daphnia magna colonies exposed to NE mucilage extract in concentrations ranging from 0 to 2000 mg/L for 48 hours. It has shown that mucilage can be classified as practically non-toxic to the Daphnia magna colonies with a LC_{50} above 500 mg/L, while the LC_{50} of COREXIT 9500 was below 2 mg/L, which is moderately toxic to the Daphnia magna colonies.

5:00pm **SS+AS+HC-MoA11 The Effect of Humidity on Chemical Interactions at Hybrid Interfaces: An In Situ Investigation of Polymer/Metal Oxide Bonds**, ***Sven Pletincx***, Vrije Universiteit Brussel, Belgium, *L. Trotochaud,* Lawrence Berkeley National Laboratory, *L.-L. Fockaert,* TU Delft, Netherlands*, A.R. Head, O. Karslıoğlu,* Lawrence Berkeley National Laboratory, *J.M.C. Mol,* TU Delft, Netherlands, *H. Bluhm*, Lawrence Berkeley National Laboratory, *H. Terryn, T. Hauffman*, Vrije Universiteit Brussel, Belgium

Probing interactions at the interface of polymer coatings and passivated metal oxide surfaces under humid conditions has the potential to reveal the local chemical environment at solid/solid interfaces under real-world, technologically relevant conditions. Common surface sensitive analysis techniques only operate under vacuum conditions, making it impossible to probe environmental effects *in situ.* Stability of formed bonds in aqueous environments between carboxylic acid functional groups of a polymer and a hydroxide surface of aluminum oxide has a great relevance to a broad range of applications. Although this region is very important for understanding adhesion of the polymer coating, it is very challenging to get useful information directly from the solid/solid interface, let alone characterize the effect of water on the formed chemical bonds.

Recent developments in the field of ambient-pressure photoelectron spectroscopy (APXPS) make it possible to set up a novel approach with respect to interface studies. [1] This is done by making the polymer layer sufficiently thin to access the interface with this surface analysis technique. A broad range of relative humidity can be simulated in the analysis chamber, to unravel interfacial chemistry changes of the hybrid system *in situ.* Here, we show that APXPS with a conventional X-ray source can be used to study the effects of water exposure on the interaction of acrylic coatings with aluminum oxide. [2]

Complementary *in situ* ATR-FTIR Kretschmann experiments on a similar model system are conducted. An Al layer is sputtered on an IR transparent crystal, the IR signal at the interface is amplified because of the Kretschmann effect and a near-interface spectrum of the oxide/polymer surface is obtained. This way, we have direct access to the interface, and the influence of an above-the-polymer electrolyte (i.e. H_2O) can be probed. An integrated setup of ATR-FTIR Kretschmann and Odd Random Phase multisine Electrochemical Impedance Spectroscopy (ORP-EIS) allows to probe the transport of water (and other ions) through the polymer towards the interface. The subsequent interface processes can be followed with infrared spectroscopy while simultaneously the protective properties of the overall hybrid system are studied by ORP-EIS. [3]

[1] D. F. Ogletree, H. Bluhm, E. D. Hebenstreit, and M. Salmeron. *Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip.*, 601, 1–2, 151–160, 2009.

[2] S. Pletincx, L. Trotochaud, L. Fockaert, J.M.C Mol, A. Head, O. Karslıoğlu, H. Bluhm, H. Terryn, T. Hauffman. *Sci. Rep.7* (45123), 2017.

[3] M. Öhman and D. Persson, *Surf. Interface Anal.*, 44, 2, 133–143, 2012.

2D Materials Focus Topic
Room: 15 - Session 2D+AS+SA+SP-TuM

2D Materials Characterization including Microscopy and Spectroscopy
Moderator: Sara Barja, Materials Physics Center, San Sebastián, Spain

8:00am **2D+AS+SA+SP-TuM1 Electronic Structure of Oxygen-Intercalated Graphene on Iridium Interface**, ***Yi Lin****, Y. Li,* Columbia University, *J. Sadowski,* Brookhaven National Laboratory, *J. Dadap, W. Jin, R. Osgood*, Columbia University, *M.S. Hybertsen*, Brookhaven National Laboratory

We report experimental and theoretical work to understand how oxygen intercalation changes the image potential state and surface state electronic structure in a metal/graphene interface. We use tunable angle-resolved two-photon photoemission spectroscopy to probe the evolution of the electronic band structure of an epitaxially grown monolayer graphene on Ir(111) as it undergoes through a cycle involving oxygen intercalation and deintercalation. Oxygen intercalation is carried out in situ and LEED is used to determine the crystallinity of the interface in the presence or absence of the intercalated oxygen. The image state manifold and its effective mass are examined. The photoemission intensity variation in momentum space and the observation of an oxygen induced state are discussed. Furthermore, a recently proposed effective potential model at the graphene/metal interface is developed further by us to accommodate oxygen intercalation and interpret our experimental electronic structure variation with good agreements.

We acknowledge support from the US Dept. of Energy, Office of Basic Energy Sciences, under Contract Numbers DE-FG 02-04-ER-46157, DE-FG02-90ER14104, and DESC0012704.

8:20am **2D+AS+SA+SP-TuM2 Graphene Moiré Pattern Ultra-High Resolution Atomic Force Microscopy**, ***Gerald Pascual****, B. Kim, K. Lee,* Park Systems Inc.

The ultra-high resolution of AFM was demonstrated in a Graphene/hexagonal Boron Nitride (hBN) sample evaluation conducted by AFM. The sample consisted of hBN substrate overlaid with a Graphene layer and was scanned under ambient air. The purpose of the evaluation was to assess the AFM ability to characterize the topography of the moiré pattern that was created when one layer was set on top of the other and offset by rotation. Using non-contact AFM mode and a standard AFM probe tip, the AFM was able to successfully image the moiré pattern super lattice constant of the sample in scans as large as 500 x 500 nm. In the higher magnification image taken at a scan size of 60 x 60 nm provides the clear evidence that not only are the super lattice constants of the moiré pattern about 15 nm [1] in width, but that the spacing between each striation on the moiré pattern is roughly 4-5 nm in length. Observations of such striations in Graphene/hBN systems have been previously reported [2]. This latter distance is in line with the expected tip radius curvature values for the AFM tip used to acquire all four sets of data.

[1] A. Zandiatashbar, B. Kim, Y. Yoo, and K. Lee, Microscopy Today 23(06):26-31 (2015)

[2] P. Gallagher, M. Lee, F. Amet et.al., Nature Comm. 7 10745 (2016)

8:40am **2D+AS+SA+SP-TuM3 Surface and Interface Properties of 2D MoS_2 and WS_2 Materials**, ***Chia-Seng Chang***, Institute of Physics, Academia Sinica, Taiwan, Republic of China*, Y.H. Lee*, National Tsing-Hua University, Taiwan, Republic of China **INVITED**

Two dimensional layered transition metal dichalcogenides (2D TMD), such as MX_2 (M = Mo, W and X = S, Se), have offered exciting new physics and chemistry, as well as potential applications in energy harvesting, electronics, and optoelectronics. Surface and interface properties of these 2D materials are fundamental to further advance them on scientific exploration and device fabrication. In this talk, we will demonstrate the growth of various TMD monolayers using ambient-pressure chemical vapor deposition. The quality of a MS_2 monolayer was examined by scanning probe microscopy, electron microscopy, and optical spectroscopy. We will discuss the key issues associated with the surfaces and interfaces of these materials.

9:20am **2D+AS+SA+SP-TuM5 Spectroscopic Investigation of Plasma-Fluorinated Monolayer Graphene and Application for Gas Sensing**, ***Hui Zhang***, Shanghai Institute of Microsystem And Information Technology, China, *J.-H. Guo*, Lawrence Berkeley National Laboratory, *X. Sun*, Soochow University

A large-area monolayer fluorinated graphene (FG) is synthesized by a controllable SF6 plasma treatment. The functional groups of FG are elucidated by various spectroscopies, including Raman, X-ray photoemission spectroscopy (XPS) and near edge X-ray absorption fine structure (NEXAFS). Raman results suggest that the defects are introduced into the monolayer graphene during the fluorination process. The fluorine content can be varied by the plasma treatment and can reach the maximum (~24.6 at% F) under 20 s plasma treatment as examined by XPS measurement. The angle dependent NEXAFS reveals that the fluorine atoms interact with the graphene matrix to form the covalent C-F bonds, which are perpendicular to the basal plane of FG. FG is applied as gas sensing material and owns much better performance for ammonia detection compared to the pristine graphene. Based on our DFT simulation results, the fast response/recovery behavior and high sensitivity of the FG gas sensor are attributed to enhanced physical absorption due to the C-F covalent bonds on the surface of FG

9:40am **2D+AS+SA+SP-TuM6 Photoemission Electron Microscopy as a New Tool to Study the Electronic Properties of 2D Crystals on Silicon Oxide**, ***Taisuke Ohta****, M. Berg,* Sandia National Laboratories, Center for Integrated Nanotechnologies, *C. Chan*, Sandia National Laboratories, *K. Keyshar,* Rice University, *G. Gupta,* University of Louisville, *P. Ajayan*, Rice University, *A. Mohite*, Los Alamos National Laboratory

The energy positions of the valence and conduction electronic states with respect to the vacuum level are essential parameters to evaluate how the band gaps of semiconductors or Fermi-levels of metals would line up with respect to each other. Defined as an energy separation between the vacuum level and the highest occupied electronic states, the ionization energy is of particular importance for atomically-thin two-dimensional (2D) crystals to predict the performance of their heterostructures useful in high performance electronics and opto-electronics. Ionization energies have been investigated based on theoretical calculations, but to the best of our knowledge, no systematic experimental confirmation is reported for the wide range of 2D crystals despite their importance.

Here, we present a new approach to study the electronic properties of prototypical 2D crystals, graphene, MoS_2, WS_2, and $MoSe_2$ monolayer and multilayer flakes, supported on thick silicon oxide (SiO_2) film using a photoemission electron microscopy combined with a deep ultraviolet (DUV) illumination. We determine the band alignments of monolayer to multilayer junctions in these four materials, and show that the ionization energy decreases from MoS_2, WS_2, to $MoSe_2$ as predicted by density functional calculations. We postulate that the defects in SiO_2 alleviate the charging of the 2D crystals thanks to the relatively low total photoemission current due to the low energy excitation by the DUV light. This study reveals a new metrology to uncover electronic properties intrinsic to 2D crystals supported on SiO_2 substrates that interact minimally with the overlying 2D crystals.

The PEEM work was performed at the Center for Integrated Nanotechnologies, an Office of Science User Facility (DE-AC04-94AL85000). T. O. is supported by the CINT user program and Sandia LDRD. The work performed by M. B. and C. C. are supported by a U.S. DOE, Office of Energy Efficiency and Renewable Energy SunShot Initiative award for BRIDGE (DE-FOA-0000654 CPS25859). K. K. was supported by the Army Research Office MURI grant W911NF-11-1-0362. A. D. M. is supported by LANL LDRD program. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

11:00am **2D+AS+SA+SP-TuM10 STM and STS Study of MoS_2/WS_2 Heterostructures Grown by Chemical Vapor Deposition**, ***Fan Zhang***, Virginia Polytechnic Institute and State University, *Z. Lu,* Tsinghua University, PR China, *H. Zheng, K. Park,* Virginia Polytechnic Institute and State University, *L. Jiao,* Tsinghua University, PR China, *C. Tao*, Virginia Polytechnic Institute and State University

2D materials like atomically thin transition metal dichalcogenides (TMDs) have received tremendous attentions for their unique properties and high potential applications. Recent developments on synthesis of 2D heterosrtuctures through the chemical vapor deposition (CVD) method provide an unprecedented opportunity to create and tune the intriguing electronic and optical properties of 2D materials such as engineering the band gaps. These 2D heterostructrues have a wide range of applications in electronics and optics, for example, tunneling transistors, single-photon emission devices and photovoltaic devices. To further optimize and design 2D heterostructures, it is essential to investigate the structural and electronic properties at the atomic scale, which is however still lacking.

In this presentation, we will focus on a high-quality MoS_2/WS_2 heterostructure grown on SiO_2 using the CVD method. Scanning tunneling microscopy (STM) and spectroscopy (STS) were performed to study the morphology and band structures of both MoS_2 monolayer and MoS_2/WS_2 heterobilayer. Atomically resolved STM images were obtained on the monolayer, heterobilayer and the interface between the monolayer and heterobilayer. The height histograms acquired respectively on the monolayer and the heterobilayer indicate that the heterobilayer is higher than the monolayer with a height difference of 0.85 ± 0.10 nm. The roughness of the monolayer and heterobilayer was for the first time quantified by STM. The root mean square (RMS) roughness of the heterobilayer is 0.253 ± 0.020 nm compared with 0.362 ± 0.031 nm of the monolayer. We also performed STS measurements on the system. Our STS results and density functional theory (DFT) calculations reveal the band gaps of the heterobilayer and the MoS_2 monolayer, which are similar to the previously reported results on MoS_2/WS_2 heterostructures fabricated through the mechanical exfoliation method.

11:20am **2D+AS+SA+SP-TuM11 Determine the Band Alignment of 2D Semiconductor Heterostructures by Photoelectron Spectromicriscopy**, *L.Y. Chang*, National Synchrotron Radiation Research Center, Taiwan, Republic of China, *Y.-X. Wang, Y.-H. Ku*, National Tsing Hua University, Republic of China, *Y.-C. Kuo, H.-W. Shiu,* ***Chia-Hao Chen***, National Synchrotron Radiation Research Center, Taiwan, Republic of China

Semiconductor heterojunction (HJ) band alignment is the most important factor for the functioning of the HJ-based devices. Therefore, the prediction and determination of the HJ band offset is always a scientifically interesting and technologically important topic. As the 2D materials emerged as the building blocks for the devices with molecular thickness, the determination of band alignment of the van der Waals HJs is becoming a critical issue.

Due to the nature of the molecular thickness and the lack of large area 2D crystal, a microscope with surface sensitivity is an ideal tool to study the fundamental properties of the 2D heterostructures.

In this regard, we have employed a synchrotron radiation based scanning photoelectron spectromicroscopy (SPEM) to study the chemical and electronic structures of the van der Waals HJs, include the single-layer transition metal dichalcogenides, and graphene/GaN HJs. In this presentation, I will report some of the band alignments of these 2D semiconductor heterostructures.

Actinides and Rare Earths Focus Topic
Room: 22 - Session AC+AS+SA-TuM

Nuclear Power, Forensics, and Other Applications
Moderator: James G. Tobin, University of Wisconsin-Oshkosh

8:00am **AC+AS+SA-TuM1 Design of Synergistic Protein-ligand Systems for f-element Coordination, where Separation, Decontamination and Nuclear Medicine Meet**, ***Rebecca Abergel***, Lawrence Berkeley National Laboratory **INVITED**

Separation of elements from the 4*f*- and 5*f*- series is a challenging task due to the similarities in their ionic radii and the existence of most of these metal ions in the trivalent oxidation state. Understanding the fundamental bonding interactions between those metal centers and selective ligands presents a rich set of scientific challenges and is critical to the development of new separation strategies as well as to a number of applied problems such as the need for decontamination after a nuclear accident or the use of radio-isotopes for new cancer treatments. Our studies utilize luminescence sensitization, UV-Visible, X-ray absorption, and X-ray diffraction spectroscopic techniques to investigate specific lanthanide and actinide coordination features by bio-inspired catecholamide and hydroxypyridinone hard oxygen-donor ligands. Using such ligands allows the solution differentiation of different metals through stabilization in specific oxidation states and provides information on their respective electronic structures. In addition, X-ray diffraction analyses using the mammalian iron transport protein siderocalin as a crystallization matrix revealed remarkable aspects of the protein's interactions with chelated metals, establishing series of isostructural systems that can be used to derive trends in the later 5*f*-element sequence, when combined with theoretical predictions. These results will be discussed with a perspective on how such studies have important implications for the use of spectroscopic and thermodynamic methods to exploit the fundamental knowledge of the role of *f*-electrons in actinide bonding for the development of new transport, separation, luminescence, and therapeutic applications.

8:40am **AC+AS+SA-TuM3 Image Processing And Particle Analysis Of Fission-Truck-Analysis In Nuclear Forensic**, ***Itzhak Halevy***, Department of Physics, NRCN, Israel, *U. Admon,* (Retiree), IAEC-NRCN, Department of Materials, Beer-Sheva Israel, *E. Chinea-Cano,* Office of Safeguards Analytical Services (SGAS), International Atomic Energy Agency (IAEA), Austria, *A.M. Weiss*, Faculty of Engineering, Bar-Ilan University, Israel, *N. Dzigal,* Office of Safeguards Analytical Services (SGAS), Austria, *E. Boblil*, Department of Physics, IAEC-NRCN, Israel

Particle analysis is a key discipline in safeguards and nuclear forensic investigations, as well as in environmental research. The radioactive Particles are usually in the micrometric size range, and intermixed within huge populations of other particles, like air-borne dust, soil, industrial exhaust pollutants or estuary sediments.

We are using the Fission Truck Analysis (FTA) technique. In that technique plastic detectors used for raping a Lexan catcher with the particles and together are radiated in nuclear reactor with thermal neutrons. The Fission Truck are trucks done by the fission products. The fission material is dominant in producing the trucks, namely the ^{235}U isotope. The Fission Truck could be more visible by special etching and can be used to locate the particles.

From that point, the analysis of Fission Truck is an image processing. Scanning the detectors is a time-consuming procedure. Automated scanning and fission star recognition will make all the Analysis easier to quantify

The challenge, therefore, consists in scanning and imaging a relatively large area detector, at a resolution of about 1µm, and locating the FT clusters while rejecting the artefacts.

Image processing was done using the Fiji distribution of ImageJ. The algorithms shown in this report were implemented using either the ImageJ macro language or the ImageJ Python scripting engine. Basic noise removal, Illumination correction and Segmentation are the basic of the imaging analysis.

I cass of large area detector a set of picture will be taken and by stiching a larg picture will be composed.

Roundness and endpoint thresholds can be adjusted to obtain fewer false negatives at the expense of more false positives. A receiver operation characteristic (ROC) can be used to characterise this.

The high and low threshold determination in the hysteresis thresholding step should be improved.

After the autometed procedure the operator can go over the FT and decide if to add stars that were not found by the software or to cancel stars that are artifact.

Correlation between forensic and image processing parameters will be defined. Even that stars are coming from ^{235}U only and it is no one to one connected only to enrichment we still think that the shape, color, number of end points and roundness can be parameters to indicates different forensic properties.

9:00am **AC+AS+SA-TuM4 Application of Linear Least Squares to the Analysis of AES Depth Profiles of Plutonium Oxides**, ***Scott Donald***, *A.J. Nelson*, Lawrence Livermore National Laboratory

Application of the linear least squares (LLS) methodology allows for quantitative determination of variation in material composition with depth, as well as permitting an understanding of differences resulting from changes in the method of preparation. LLS fits were applied to decompose and enhance the interpretation of spectra obtained by Auger electron spectroscopy (AES) during depth profiles of oxidized plutonium surfaces. By means of the LLS algorithm, chemical state assignments of the Pu $P_1VV/O_{45}VV$, O KLL, and C KLL Auger transitions were determined and the existence of a subsurface oxy-carbide layer was identified, with confirmation provided from comparison to previous measurements of standard samples.

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

9:20am **AC+AS+SA-TuM5 Physical and Chemical Characterization of Solid Pu and Np Sources after Multi-year Exposure to Environmental Conditions**, ***Brian Powell***, Clemson University **INVITED**

A field scale radionuclide vadose zone transport experiment at the United States Department of Energy Savannah River Site is being operated by Savannah River National Laboratory and Clemson University scientists. In this experiment, plutonium and neptunium solid sources are buried in 61 cm long x 10 cm diameter lysimeters which are open to precipitation. Such experiments provide the opportunity to observe changes in the microcrystalline structure of plutonium and neptunium solid phases under various environmental conditions. In the current experiments, sources of neptunium and plutonium in multiple initial oxidation states and chemical forms have been deployed for 2-5 years of field exposure. These sources include $Pu(V)NH_4CO_3(s)$, $Pu(IV)(C_2O_4)_2(s)$, $Pu(III)_2(C_2O_4)_3(s)$, $Pu(IV)O_2(s)$, $Np(IV)O_2(s)$ and $NpO_2NO_3(s)$. X-ray absorption spectroscopy (XAS) analysis of initially $Pu(V)NH_4(CO_3)$ sources archived in an inert atmosphere and sources exposed to lysimeters indicate some reduction to Pu(IV) within the sources leading to the formation of $Pu(IV)O_2(s)$. Thus, there appears to be an auto-reduction of $NH_4Pu(V)CO_3(s)$ to $Pu(IV)O_2(s)$ even under inert conditions. However, solvent extraction on archived and field-deployed sources show the archived source still contains around 40% Pu(V) whereas the same source from a field lysimeter deployed for 2.5 years contained less than 10% of Pu(V). XAS and electron microscopy studies have demonstrated differences between $Pu(IV)O_2(s)$ formed via reduction of $Pu(V)O_2NH_4CO_3$ and initially $Pu(IV)O_2$ formed from precipitation of a Pu(IV) solution. The behavior of initially $Np(IV)O_2$ sources was quite different showing oxidation to Np(V) and subsequent downward transport of more soluble $Np(V)O_2^+$. The oxidation of $Np(IV)O_2(s)$ leads to formation of a much more disordered solid phase with a significantly altered morphology than the initial $Np(IV)O_2(s)$. The results of these experiments will be discussed in terms of evaluating the history of the sample through analysis of the microcrystalline structure and the influences of aging under various environments.

11:00am **AC+AS+SA-TuM10 Synchrotron Radiation Investigation of f-element Extraction from a Carboxylic Acid Functionalized Porous Aromatic Framework**, ***David Shuh***, Lawrence Berkeley National Laboratory, *S. Demir, N.K. Brune,* University of California Berkeley, LBNL, *J.F. Van Humbeck, J.A. Mason,* University of California Berkeley, *T.V. Plakhova,* Lomonsov Moscow State University, Russia, *S. Wang,* University of California Berkeley, LBNL, *G. Tian, S.G. Minasian, T. Tysliszczak,* Lawrence Berkeley National Laboratory, *T. Yaita, T. Kobayashi,* Japan Atomic Energy Agency, *S. Kalmykov,* Lomonsov Moscow State University, Russia, *H. Shiwaku,* Japan Atomic Energy Agency, *J.R. Long,* University of California Berkeley

Porous aromatic frameworks (PAFs) incorporating a high concentration of acid functional groups possess characteristics that are promising for use in separating lanthanide and actinide metal ions, as required in the treatment of radioactive waste. These materials have been shown to be indefinitely stable to concentrated acids and bases, potentially allowing for multiple adsorption/stripping cycles. Additionally, the PAFs combine exceptional features from metal organic frameworks (MOFs) and inorganic/ activated carbons giving rise to tunable pore surfaces and maximum chemical stability. The adsorption of selected metal ions, Sr^{2+}, Fe^{3+}, Nd^{3+}, and Am^{3+}, from aqueous solutions employing a carbon-based PAF, BPP-7 (Berkeley Porous Polymer-7) has been investigated. This material displays high metal loading capacities together with excellent adsorption selectivity for neodymium over strontium. X-ray absorption spectroscopy studies show that the stronger adsorption of neodymium is attributed to multiple metal ion and binding site interactions resulting from the densely functionalized and highly interpenetrated structure of BPP-7. Recyclability and combustibility experiments demonstrate that multiple adsorption/stripping cycles can be completed with minimal degradation of the polymer adsorption capacity.

11:20am **AC+AS+SA-TuM11 The Effect of Al_2O_3 Encapsulation Using Atomic Layer Deposition on the Photoluminescent, Water and Thermostability Properties of $SrAl_2O_4$ Based Phosphors**, ***Erkul Karacaoglu***, *E. Özturk,* Karamanoglu Mehmetbey University, Turkey, *M. Uyaner,* Selcuk University, Turkey

Aluminate based phosphors (MAl_2O_4, $M_4Al_{14}O_{25}$, M= Sr, Ba, Ca, etc.) are chemically unstable against water and even moisture. Moreover, some of phosphors, like green emitting phosphorescent materials' luminescence properties, but not their structural properties, are affected negatively during reheating applications because the 2+ ionic state of europium is oxidized to 3+ in open atmosphere low temperature heating process thus limiting their applications. Their hydrolysis process were studied and analyzed intensively by researchers. Changes of pH value of suspensions, the structures and optical properties of the hydrolysis of phosphor structures had been investigated. In this research, to prevent or minimize this degradation, to enhance the water resistance and to maintain the phosphorescence properties, an Al_2O_3 coating on the surface of $SrAl_2O_4$ based phosphor pellets (1 mm thickness) were prepared using Atomic Layer Deposition (ALD) method with Trimethylaluminum (TMA) precursor. The investigation of phase formation of strontium aluminate was analyzed by thermal analysis (DTA/TG) until 1500 °C. The $SrAl_2O_4$ with Monoclinic structure in single phase having lattice parameters a=8.44365 Å, b=8.82245Å, c=5.15964Å and α=90° β=90° γ=90° were obtained according to XRD analysis. The photoluminescence (PL) results of both open and reduced atmosphere synthesized phosphors with excitation and emission wavelengths and decay time were determined by a PL spectrometer at room temperature. The reduced and open atmosphere synthesized samples have different photoluminescent characteristics because of ionic state of europium in 2+ and 3+ at reduced atmosphere and open atmosphere, respectively. Moreover, it was obtained that the main crystal, $SrAl_2O_4$, had photoluminescent properties. The surface analysis of phosphors as morphology and elemental analysis (SEM/EDX), X-ray diffraction (XRD), water and heat resistance (thermostability), photoluminescence (PL) of the phosphors before and after encapsulation were discussed in detail.

Applied Surface Science Division
Room: 13 - Session AS+MI+SS-TuM

Quantitative Surface Analysis: Effective Quantitation Strategies

Moderators: Kateryna Artyushkova, University of New Mexico, Gregory L. Fisher, Physical Electronics

8:00am **AS+MI+SS-TuM1 Effective Attenuation Lengths for Different Quantitative Applications of XPS**, *A. Jablonski,* Institute of Physical Chemistry, Warsaw, Poland, ***Cedric Powell***, NIST

The effective attenuation length (EAL) is a convenient parameter for use in place of the inelastic mean free path (IMFP) to account for elastic scattering of signal photoelectrons in XPS. The most common EAL application is measuring the thicknesses of overlayer films on planar substrate from the attenuation of substrate photoelectrons in laboratory XPS systems. EALs for this purpose can be obtained from a NIST database [1] and from empirical predictive equations [2]. In addition, EALs can be defined for other quantitative applications of XPS with laboratory XPS systems: (i) determination of thicknesses of overlayer films on planar substrates from changes of intensities of overlayer photoelectrons [3]; (ii) quantitative determination of surface composition by XPS [4]; and (iii) determination of shell thicknesses of core-shell nanoparticles [5]. Finally, EALs have been determined for measuring thicknesses of overlayer films on planar substrate from the attenuation of substrate photoelectrons in XPS with linearly polarized X-rays with energies up to 10 keV [6]. These EALs will be compared to corresponding EALs for unpolarized X-rays [2,6]. The EAL is not a simple material parameter like the IMFP but depends on the defining equation for the particular application as well as on the experimental configuration.

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8:20am **AS+MI+SS-TuM2 Plumbing the Depths using the XPS Inelastic Background**, ***Alexander Shard***, *S.J. Spencer*, National Physical Laboratory, UK

A novel semi-empirical description of the intensity of inelastically scattered electrons in XPS is introduced. The functional form describes the background over the full energy range of an XPS survey spectrum and is not intended to be used as a background subtraction method. Therefore, it may be used even in the absence of elastic peaks in the spectrum. Samples of gold and silicon oxide coated with defined thicknesses of Irganox 1010 and a calibrated XPS spectrometer were used to generate reference data. These data were used to establish appropriately linked functions for substrate and overlayer background shapes as a function of overlayer thickness and the known relative intensities and energies of the pure materials. A common functional form could be found and appears to be of general utility, at least for organic overlayers. The description shows that the measurement of overlayer thicknesses well beyond the traditional XPS information depth is possible, for organic layers on gold this can be larger than 50 nm. In principle, the background shape of any substrate beneath an organic overlayer can be described and the thickness adjusted to match experimental data.

This description of XPS background shapes may be employed to rapidly confirm the chemistry and depth of substrate materials. Discrepancies with thicknesses established by traditional analyses of elastic peak intensities can be employed to measure defect densities in coatings. The use of background shape analysis should also be useful for measuring the overlayer thickness on topographic materials where traditional angle-resolved analysis is not appropriate. Furthermore, these descriptions should be useful for new developments in XPS, such as nanoparticle shell measurement, high energy XPS and near-ambient pressure XPS.

8:40am **AS+MI+SS-TuM3 Quantitative Organic Depth Profiling and 3D Imaging using Secondary Ion Mass Spectrometry**, ***Rasmus Havelund***, National Physical Laboratory, UK **INVITED**

The development of gas cluster ion beams has transformed the ability for depth profiling of organic materials using secondary ion mass spectrometry (SIMS). The technique now permits molecular information to be obtained with excellent depth resolution to depths of several μm. This type of analysis is highly valuable across a range of applications but quantitative analysis continues to be a major challenge.

Carefully prepared organic reference multi-layers have in a number of studies been used to measure gas cluster ion sputtering yields[1,2], depth resolutions[1,2], and, recently, the matrix effect in binary molecular mixtures[3]. These parameters are important in any attempt to achieve quantification. Here, the ability to accurately measure the thickness of organic layers and the depth of interfaces is evaluated using such organic reference multi-layers. The depth of interfaces is needed for materials or devices consisting of distinct layers of pure single materials where a measurement of the thicknesses of the layers provides, quantitatively, the amount of substance in the layers. In sputter depth profiling, the thickness of a layer will be reflected in the primary ion dose required to remove the layer, and in the integrated characteristic secondary ion signal intensity through that layer. A detailed analysis of the critical role of the matrix effect on these parameters is provided, and the prospects for measuring compositions in mixed materials are discussed based on results from three different sample systems. This provides useful information for the development of quantification strategies.

[1] Niehuis et al., Surface and Interface Analysis, 45, 158-162, 2013

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[3] Shard et al., International Journal of Mass Spectrometry, 377, 599-609, 2015

9:20am **AS+MI+SS-TuM5 Coupling Effects on the Intensity and Background of the Cr 3*p* Photoemission Spectrum around the Cr 2*s* Threshold**, ***Alberto Herrera-Gomez,*** CINVESTAV-Unidad Queretaro, Mexico, *D. Cabrera-German,* Universidad de Sonora, *F.-S. Aguirre-Tostado,* CIMAV-Monterrey, *A. Dutoi,* University of the Pacific, *M.-O. Vazquez-Lepe,* Universidad de Guadalajara, *P. Pianetta,* Stanford University, *D. Nordlund,* Stanford Synchrotron Radiation Lightsource, *O. Cortazar-Martínez, L. Gomez-Muñoz,* CINVESTAV-Unidad Queretaro, Mexico, *A. Torrea-Ochoa,* CINVESTAV-Unidad Queretaro

By describing the photoelectric phenomenon as the absorption of a photon by a core electron and its subsequent emission, it is possible to understand many of the features found in XPS data ... as long as the photon energy is far away from the threshold of deeper core levels. For these cases, “the independent particle approximation, which had been thought to be applicable to atomic photoionization cross sections well above threshold, is clearly not applicable.”[1,2] Even at energies away from deeper thresholds, quantification of the composition can be done only if we are also willing to employ empirical background subtraction methods such as the Shirley function to assess peak intensities. Through this method, employed in conjunction with others methods accounting for the background due to inelastic scattering (i.e., Tougaard background), it is possible to properly reproduce the experimental background [3] and assess the composition of surfaces. Of course, the intensity related to the background is ignored for composition calculations. Ignoring the background due to inelastic scattering is perfectly self-consistent because these electrons are effectively accounted by the Debye-Waller attenuation factor calculated from the inelastic mean free path. However, there is not any attenuation factor to account for the ignored Shirley electrons.

Through the study of the peak intensity of the Cr 3*p* peak with photon energies around the Cr 2*s* threshold, we found that these two issues, 1) channeling effects on the peak intensity and 2) the need to ignore the Shirley electrons for composition calculations, are, in fact, related. The behavior of the Cr 3*p* background strongly suggest coupling between the 3*p* and the valence states. These coupling most exist for a brief time after photon absorption, and the observed photoelectrons should actually come from one of these coupled states. That is, “describing the photoelectric phenomenon as the absorption of a photon by a core electron and its subsequent emission” is not the complete paradigm for photoemission.

[1] E.W.B. Dias, H.S. Chakraborty, P.C. Deshmukh, S.T. Manson, Breakdown of the Independent Particle Approximation in High-Energy Photoionization, (1997) 4553–4556.

[2] W. Drube, T.M. Grehk, S. Thieß, G.B. Pradhan, H.R. Varma, P.C. Deshmukh, S.T. Manson, Pronounced effects of interchannel coupling in high-energy photoionization, 46 (2013). doi:10.1088/0953-4075/46/24/245006.

[3] A. Herrera-Gomez, M. Bravo-Sanchez, F.S. Aguirre-Tostado, M.O. Vazquez-Lepe, The slope-background for the near-peak regimen of photoemission spectra, J. Electron Spectros. Relat. Phenomena. 189 (2013) 76–80. doi:10.1016/j.elspec.2013.07.006.

9:40am **AS+MI+SS-TuM6 Using Main Peak Intensities for XPS Quantitation: Strengths, Weaknesses, Issues**, ***B. Vincent Crist,*** XPS International LLC, *C.R. Brundle,* C. R. Brundle and Associates

It is common, in the practical world, to use the most intense XPS peaks from survey spectra, in combination with instrument software RSF’s, for atom percent quantitation. The advantage is obvious: time saved. Occasionally, peak overlaps force the use of a secondary peak plus a ratio of RSF’s. The origin of that ratio is usually based on theoretical cross-sections, σ (1), corrected for transmission function, T, and escape depth, λ.

Using clean elemental surfaces the validity of using relative σ’s for peaks in the spectrum was tested. Some large discrepancies were found. The same occurred for some crystal materials and bulk polymers. Two possible causes are errors in σ’s, or variations in intensity losses to satellites, invalidating the use of main peak intensities plus σ values (σ includes intensity from all final states). σ values should be good to better than 10% error (1). Intensity losses can vary with core level, but there are examples here where this does not seem to be the problem.

Suppliers’ RSF’s come either from theoretical σ’s (1), or from empirical standards (2) where only main peaks are included. Except for 1st row elements there are significant discrepancies (>30%) between the approaches. We discuss possible reasons and note:

(a) the suppliers’ empirical standard based RSF’s all seem to be derived from the data of Wagner, et al. (2). That Herculean study included results from other studies on a range of poorly characterized instruments and samples whose surface compositions might be suspect.

(b) The discrepancies cannot be explained by the lack of inclusion of satellite intensities for the standards approach, as any correction generally worsens agreement.

We conclude it is time for a reexamination of the standards approach with modern instruments and better controlled samples. It is now possible to theoretically estimate the fraction of total intensity lost to satellites (3) and so to establish what fraction of σ should be used when relying on main peak intensities.

1 J. H. Scofield, J. Elec. Spec. 8, 129 (1976)

2 C. D. Wagner, et al, Surface Interface Analysis, 3, 211, (1981)

3 P. S. Baguset al., J. Chem. Phys., in press (2017).

11:00am **AS+MI+SS-TuM10 XPS Spin-Orbit Splitting; Multiplet Splitting; Shake-up Losses: Implications for Determining Covalent Interactions and for Quantitative Analysis**, ***C. Richard Brundle,*** C.R Brundle & Associates, *P.S. Bagus,* University of North Texas

The “apparent” spin-orbit (S-O) splitting of metal cation core levels, observed by XPS for 3d transition metals, can vary with the ligand (anion) concerned, [1], even though true S-O splitting is an atomic property not depending on the atom’s environment. However, multiplet splittings of the core-level XPS of 3d cations depend on 3d shell occupation [1-3], so variation in this can alter the apparent S-O splitting. Such variation should have a consequence on the relative positions of the no-loss S-O component peak positions (ie the XPS “apparent” S-O splitting), via the well-established Mann and Aberg Sum Rule. [4]. Here we establish the importance of a mechanism that also contributes to changes in the multiplet splitting, and so in the apparent S-O splitting. This mechanism is covalent mixing of metal cation and ligand orbitals (for example Ref [5]), which alters the exchange integrals between core and valence electrons.

For a closed 3d shell, eg Ti^{4+} there is no possibility of multiplet splitting, but an apparent discrepancy in the S-O component intensity ratio has been reported (1), and an explanation proposed involving different intensity losses to shake-up satellites from each component. Our calculations indicate identical intensity losses, however, and a reanalysis of the experimental data indicates that the correct intensity ratio can be recovered by simply including the lifetime broadening of the $2p_{1/2}$ component, which results in overlap between it and the $2p_{3/2}$ component.

We present theoretical evidence, bare cation and cluster calculations, which provide quantitative estimates of the importance of various mechanisms for the covalency and for changes in apparent S-O splitting. These calculations allow comparison of “apparent S-O splitting” to “true” S-O splitting, the latter defined as the difference of the relativistic orbital energies of the S-O split levels. Furthermore, they permit establishing the differing importance of covalency for different ligands, and thus a connection to the observation of differences in core-level XPS for different ligands [6]. These effects also have a consequence for quantitative analysis using the 2p and 3p cation XPS peaks, which will be discussed.

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2. R. P. Gupta and S. K. Sen, Phys. Rev. B , 71 (1974)

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4. R. Manne and T. Åberg, Chem. Phys. Lett. , 282 (1970)

5. P. S. Bagus, E. S. Ilton, and C. J. Nelin, Surf. Sci. Rep. , 273 (2013)

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11:20am **AS+MI+SS-TuM11 The Cu *2p* Photoemission Spectra from Mixed Oxidation States**, ***Jorge-Alejandro Torres-Ochoa***, CINVESTAV-Unidad Queretaro, Mexico, *D. Cabrera-German,* Universidad de Sonora, Mexico, *M. Bravo-Sanchez,* Instituto Potosino de Investigación Científica y Tecnológica A.C, Mexico, *A. Herrera-Gomez,* CINVESTAV-Unidad Queretaro, Mexico

Some X-ray photoelectron spectra have complicated structures that makes the peak fitting procedure difficult, especially with transition metals. Recent studies have shown the need to fit both branches of the *2p* spectra such as in Fe [1] and Co [2] This proved that modeling both branches concurrently is necessary to avoid errors such as area underestimation. In this report, copper films were obtained by sublimation in ultra-high vacuum ($5.5x10^{-8}$ torr) on Si(100) substrates. Immediately after deposition, the films were characterized by X-ray photoelectron spectroscopy using a monochromatic Al Kα source (hv=1486.7 eV). To study the initial stages of oxidation, the films were heat treated in an ultra-high purity oxygen atmosphere at 200 °C from 1 to 10 min.

From the photoemission spectrum, it was possible to observe three coexisting copper species. Using the Active Background Method,[3] an accurate fit was achieved for Cu *2p*. Both chemical species, Cu^{1+} (932.5 eV) and Cu^{2+} (933.5 eV), together with their satellites (Cu^{1+}: 946.5 eV, Cu^{2+}: 941.1 eV, and Cu^{2+}; 943.9 eV) were clearly identified.[4] The fit required two extra peaks at 934.7 eV and 942.4 eV. There is evidence that these peaks correspond to Cu^{3+}.

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11:40am **AS+MI+SS-TuM12 Quantifying Valence Band Offsets at Metal\($(Hf,Zr)O_2$ Interfaces for Ferroelectric Devices**, ***Michael Brumbach****, S. Smith, M.D. Henry, J. Dickerson, D. Robinson Brown, J. Ihlefeld,* Sandia National Laboratories

The compatibility of HfO_2 deposition with current silicon microelectronic processing make it an appealing alternative to traditional ferroelectrics. A variety of applications, including Tunneling Electroresistance devices, can benefit from the switchable polarization of HfO_2-based thin films, first reported in 2011. In these devices the optimal band-alignment for electron transport is dependent on selection of top and bottom contact materials. In this work, the valence band offset of $(Hf,Zr)O_2$ with a number of metal contacts has been quantified by X-ray photoemission measurements. Coupled with experiment, simulations have been performed to identify the band offsets for successful device operation. Metal contacts investigated include Pt, Ni, Au, Al, Ta, and TaN. For some metal films there is the experimental consideration for the impact of air oxidation on the measured valence band offsets. In addition to characterizing films in a bottom-up approach, the metal layers were ion milled to thin the overlying metal and reveal the interfacial boundary. In such cases, the oxide was removed and valence band offset values were measured. The role of differential sputtering in mono-atomic and the application of gas cluster ion sputtering to alleviate differential sputtering will be discussed. Additional techniques including inverse photoemission, UV-photoemission, and Kelvin probe will be presented for further quantification of the valence band offsets.

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12:00pm **AS+MI+SS-TuM13 Quantitative Peak-Fitting Analysis of the Photoemission Spectra of Metallic Zinc and Zinc Oxide Films**, ***Dagoberto Cabrera-German****,* Universidad de Sonora, Mexico, *G. Molar-Velazquez, G. Gómez-Sosa,* CINVESTAV-Unidad Queretaro, Mexico, *W. De la Cruz,* Universidad Nacional Autónoma de México, *A. Herrera-Gomez,* CINVESTAV-Unidad Queretaro, Mexico

The quantitative analysis of the X-ray photoelectron spectra of Zn and ZnO is a challenging task due to plasmon-loss features and small binding energy shifts that lead to inaccurate results on the assessment of the chemical state of mixed systems of metallic zinc and zinc oxide.[1] Additionally, the Zn 2*p* spectra hold a complex background that traditional background modeling methods are unable to reproduce accurately.

We have analyzed the Zn 2*p* and O 1*s* spectra of a metallic Zn film that has been subject to pressure and time controlled oxidations at high vacuum. Through the state-of-the-art peak-fitting methods[2–4] we have overcome the difficulties, as mentioned earlier, of performing a quantitative analysis of a metal and oxide system and we have also noted several interesting features of the Zn 2p spectrum.

We found that the assessed chemical composition for several oxygen exposures is $ZnO_{1.00\pm0.10}$, this suggests that the set of peak parameters employed to resolve the metallic and oxide photoemission signals, are accurate and can be applied in quantitative studies.

The main characteristic of the peak-fitting procedure is that close experimental data reproduction requires an individual assignment of Shirley backgrounds for each peak comprising the spectra. Therefore an accurate quantitative analysis can only be done employing the Shirley-Vegh-Salvi-Castle (SVSC) background under the active approach.[2–4]

Another feature is that the intensity of plasmon-peaks and their background are not accurately described by any existing energy loss (intrinsic and extrinsic) formalism. In fact, the modeling of their background trend requires the addition of an intense Shirley contribution, up to 10 times larger than the Shirley contribution of the main photoemission line. These are outstanding results that suggest that these plasmon-peaks are produced by a loss process that remains unaccounted.

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

Probing Chemical Reactions at the Nanoscale

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

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

Single molecules are possible components of miniaturized electronic devices. Interconversion between states using external stimuli is a convenient way to generate single molecule devices such as switches and sensors. In this study, we have devised an electromechanical single molecule junction where molecular orientation is controlled by the working electrode potential in an electrochemical environment. We used the scanning tunneling microscopy (STM)-break junction method to measure the electrical properties of benzene derivatives, e.g., tetrafluoroterephthalic acid (TFTPA), terephthalic acid (TPA) and trimesic acid (TMA), bridged between two gold electrodes (the conducting substrate and STM tip). At potentials more negative than zero charge potential, direct contact between the π –system of a benzene ring and the Au (111) electrode results in the formation of a highly ordered monolayer and a high conductance of 0.24 $G_{\circ}$, 0.22 $G_{\circ}$ and 0.15 $G_{\circ}$ are detected for TFTPA, TPA and TMA, respectively. Moving to potentials more positive than the potential of zero charge triggers an order-disorder transition as revealed by STM. Our results show that charge transport through the π conjugated benzene ring increases by fluorination of TPA and decreases by an addition of a carboxylic acid functional group to the TPA. Accordingly, these results suggest that using functional groups, charge transport can be modified by manipulation of the electronic structure of molecules.

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

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

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

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

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

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

References:

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11:20am **SP+AS+MI+NS+SS-TuM11 Nanoscale Chemical Analysis with Photo-induced Force Microscopy**, ***Sung Park***, Molecular Vista, Inc.

Infrared Photo-induced Force Microscopy (IR PiFM) is based on an atomic force microscopy (AFM) platform that is coupled to a widely tunable mid-IR laser. PiFM measures the dipole induced at or near the surface of a sample by an excitation light source by detecting the dipole-dipole force that exists between the induced dipole in the sample and the mirror image dipole in the metallic AFM tip. This interaction is strongly affected by the optical absorption spectrum of the sample, thereby providing a significant spectral contrast mechanism which can be used to differentiate between chemical species. Due to its AFM heritage, PiFM acquires both the topography and spectral images concurrently and naturally provides information on the relationship between local chemistry and topology. Due to the steep dipole-dipole force dependence on the tip-sample gap distance, PiFM spectral images have spatial resolution approaching the topographic resolution of AFM, demonstrating sub 10 nm spatial resolution on a variety of samples. PiFM spectral images surpass spectral images that are generated via other techniques such as scanning transmission X-ray microscopy (based on synchrotron source), micro confocal Raman microscopy, and electron microscopes, both in spatial resolution and chemical specificity. The breadth of the capabilities of PiFM will be highlighted by presenting data on various organic, inorganic, and low dimensional materials. By enabling imaging at the nm-scale with chemical specificity, PiFM provides a powerful new analytical method for deepening our understanding of nanomaterials and facilitating technological applications of such materials.

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

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

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Applied Surface Science Division
Room: 13 - Session AS+TF-TuA

Problem Solving Using Surface Analysis in the Industrial Laboratory

Moderators: Jeffrey Fenton, Medtronic, Paul Vlasak, The Dow Chemical Company

2:20pm **AS+TF-TuA1 TOF-SIMS MS/MS for Industrial Problem Solving**, *G.L. Fisher, D.M. Carr,* Physical Electronics, *T. Miyayama, S. Iida,* ULVAC-PHI, Japan, ***Scott Bryan***, Physical Electronics

One of the most common requests in an industrial analytical lab is to distinguish between "good" and "bad" samples of supposedly the same composition. For failure analysis labs, the goal is often to determine the source of contamination or defects in a production process with poor yield. Identifying contamination left behind from different cleaning procedures or after extended use is also a common request. In all these circumstances, one does not know ahead of time what chemical compounds are present. TOF-SIMS is an ideal technique for these applications because it has high sensitivity, high specificity, and parallel detection of all masses. One complication is that real-world samples usually have a complex mixture of compounds on the surface, making the TOF-SIMS spectrum difficult to interpret. Further, the use of a wide variety of different primary ion beams (e.g. Ga^+, In^+, Au^+, Bi^+, C_{60}^+, and Ar_n^+) has complicated the use of TOF-SIMS spectral databases for compound identification due to large changes in relative peak intensities from one beam to another.

A MS/MS capability was recently integrated into a TOF-SIMS instrument to make compound identification easier [1,2]. It allows unambiguous identification of both organic and inorganic peaks above *m/z* 200, where the mass accuracy is insufficient to identify the composition of a peak by its exact mass. A MS/MS spectrum from a single precursor mass is much easier to match using a spectral database compared to using the original complex TOF-SIMS spectrum. In addition, the MS/MS spectrum of a given precursor ion is independent of the primary ion used to generated it.

Several case studies will be given where MS/MS was needed to identify compounds from an analysis of industrial samples. Two modes of MS/MS will be compared and contrasted. One is based on collision induced dissociation (CID) with inert gas and the other is based on post source decay (PSD).

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2:40pm **AS+TF-TuA2 *In Situ* Molecular Imaging of Switchable Ionic Liquids**, ***Juan Yao***, *D. Lao, X.F. Yu, S. Nune, D. Heldebrant, Z.H. Zhu, X.Y. Yu,* Pacific Northwest National Laboratory

Switchable ionic liquids (SWILs) are emerging green solvents in industry for cleaner separation and efficient biomass production, for instance. However, the liquid structure and composition of SWILs are not fully understood. Besides some off-line analyses using NMR and IR, our knowledge of the SWIL is quite limited. We used in situ liquid time-of-flight secondary ion mass spectrometry (ToF-SIMS) to study SWILs in this work. SWILs are introduced into a vacuum compatible microfluidic channel for analysis by liquid SIMS. Two model systems have been investigated. The first consists of 1, 8-diazabicycloundec-7-ene (DBU) and 1-hexanol with different CO_2 loadings. The second is primarily made of koechanol with various CO_2 loadings. Koechanol acts as both acid and base in the latter. Our results show two coexisting liquid phases in the two SWIL systems. This phenomenon was only hypothesized in previous theory prediction. We are able to provide the first physical evidence of the complex liquid-liquid interface using three-dimensional chemical mapping with submicrometer resolution. In addition, more complex stoichiometry is discovered as a result of SWIL formation. More importantly, we provide the first chemical spatial mapping elucidating the evolved liquid-liquid interface as a result of SWIL formation. We anticipate the more detailed molecular level understanding of the liquid structure and composition are instrumental to build the foundation for predicative material synthesis and more versatile industrial applications.

3:00pm **AS+TF-TuA3 Employing a Surface and Bulk Analytical Approach for the Synthesis and Characterization of Ophthalmic Biomaterials**, ***Daniel Hook***, *A. Hoteling, W. Nichols, I. Nuñez, K. Wygladacz*, Bausch + Lomb, Inc. **INVITED**

Background:

During the development of a new soft contact lens material three areas of focus; regulatory requirements, manufacturing requirements and customer needs, are often used to guide the overall activities of the material development process.

Regulatory requirements are associated with material properties that are collected using methods defined by standards organizations and accepted by regulatory bodies globally. While this data is mandatory for the registration and approval of a contact lens material it is incomplete in that it only defines the basics of the material.

Manufacturing requirements such as speed of polymerization and completeness of reaction provide critical information so that an effective material can be made in a cost effective manner.

Finally, patients will demand a material that can be worn comfortably while correcting vision over the course of the wearing schedule. Patient focused parameters such as incorporation of wetting agents that create a wettable surface as well as a robust surface that will withstand handling of the course of several weeks of wear area also critical to success.

Methods:

The ISO methods 18369-4:2006, 4.6, 18369-4:2006, 4.4, 18369-4:2006, 4.5 were used to collect bulk properties of water content, oxygen permeability and refractive index while ANSI method Z80.20.2010, 7.10 was used to collect captive bubble contact angle data (CBCA). Photo-Differential Scanning Calorimetry (Photo DSC), Gas Chromatography-Mass Spectrometry (GC-MS) and Liquid Chromatography - Mass Spectrometry (LC-MS) were used to measure polymerization kinetics and monomer consumption. X-ray Photoelectron Spectroscopy (XPS) data was collected to understand surface uniformity and product consistency while Atomic Force Microscopy (AFM) was used to assess surface morphology over the course of the wearing schedule.

Results and Conclusion:

Data summarizing the submission for samfilcon A, a 46% water, 114 Dk material will be presented. CBCA coupled with XPS data will demonstrate a consistent surface wettability and chemistry across multiple lens powers and lens lots. Photo DSC, GC-MS and LC-MS will illustrate how the lens polymerizes in two distinct time resolved phases enabling the incorporation of polyvinyl pyrrolidone wetting agent into the lens bulk and surface. Together the analytical data will provide a unique picture of the data set needed for regulatory approval along with satisfying the manufacturing requirements and patient needs for a successful ophthalmic biomaterial.

4:20pm **AS+TF-TuA7 Surface Properties and Interfacial Bonding of Anodic Aluminium Oxides and Organic Resins**, ***Shoshan Abrahami***, *T. Hauffman,* Vrije Universiteit Brussel (VUB), Belgium, *De KoK,* Fokker Aerostructures BV, Papendrecht, The Netherlands, *Gudla, Ambat,* Technical University of Denmark (DTU), Denmark, *J.M.C. Mol*, TU Delft, Netherlands, *H. Terryn*, Vrije Universiteit Brussel, Belgium

Aluminium pretreatment for bonding purposes needs to produce a stable oxide with optimal chemical and structural characteristics for adhesion with the organic resin. Contributions at the interface region can be related to adsorptive interactions as well as mechanical interlocking between the two phases. To separate between these two effects, we applied either barrier-type or porous-type oxides on two sets of specimens. This paper presents an overview of a study on the relation between oxide properties and interfacial bonding, as affected by the nature of electrolyte and the anodizing conditions, as well as changes in the chemistry of the organic resin (epoxy, phenol, silanes). A detailed characterization of different anodic oxides and its effect on the adsorption of resin-derived functional molecules was performed using X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). Results indicate significant changes in the chemical composition of the oxides as a function of the electrolyte[1]. Mechanical peel test performance indicate that the initial bond strength is independent of the oxide surface chemistry, while the stability under the ingress of water is correlated to the amount of surface hydroxyls[2]. The presence of phosphates and sulphates did not alter bonding mechanisms, only the availability of hydroxyls. Further, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are used to characterize the geometrical modifications to the pore- and oxide structure in porous-type oxides. In addition, energy-dispersive X-ray spectroscopy (EDS) profiles were acquired on TEM cross-sections to assess the oxide structure and concentration of resin inside the pores. Linking these morphological features to peel results show that two types of modifications are crucial for the formation of a strong and durable bonding[3]. A minimum pore size is needed for the resin to fill the oxide pores for good initial adhesion. Surface roughness, on the other hand, was found beneficial for the durability of the bond upon the ingress of water. Overall, the results demonstrate that both surface chemistry and oxide morphology contribute to the strength and durability of an adhesive bond.

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2. Abrahami, S. T., et al., Effect of Anodic Aluminum Oxide Chemistry on Adhesive Bonding of Epoxy. J. Phys. Chem. C 2016, 120, 19670-19677.

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4:40pm **AS+TF-TuA8 Practical Considerations of Different Ion Sources for Industrial Applications: The Good, the Bad, and the Indifferent**, ***William Stickle***, *C.N. Young*, *M.D. Johnson*, HP Inc., *B. Schmidt*, Physical Electronics USA

In recent years advances in ion gun technology have resulted in the routine application of cluster ion sources for analyses in industrial R&D labs. Most industrial laboratories study a wide variety of material systems ranging from polymers to inorganic thin films; many of these material systems require analysis not just of the as received surface, but also of and through the depth of a thin film. The purpose of this talk is to compare and contrast the benefits and drawbacks of performing routine XPS analyses using a mono atomic argon ion source compared with a C_{60}^+ ion source and an argon gas cluster ion source. From a practical standpoint, i t is important to understand the sputter induced chemistry that may be created by these various sources and the trade-offs for applying these different primary ion sources for routine surface chemical analyses. The effects of preferential sputtering and chemical changes or reactions of metal oxides will be discussed. Several different material systems are examined and discussed by comparing the information obtained using mono atomic argon, an argon gas cluster source and a C_{60}^+ ion source for enhancing and clarifying 'routine' analyses. The different types of samples to be discussed will include polymers, fluoropolymer systems, amorphous metals and their oxides and multilayer thin films.

5:00pm **AS+TF-TuA9 Surface Analysis in an Industrial Setting: Non-ideal Real World Samples**, ***Vincent Smentkowski***, General Electric Global Research Center **INVITED**

The top few nanometers of a sample is defined as the surface. The surface is where most chemical reactions take place. There are many instances where the surface of materials are designed/functionalized in order to optimize properties and improve device performance; there are other instances where the surface becomes compromised and the material/device performance degrades following treatment and/or use. Accurate characterization is essential in order to understand material/device performance.

Auger Electron Spectroscopy (AES), X-ray Photoelectron Spectroscopy (XPS), Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and Scanning Probe Microscopy (SPM) are the most common, and commercially available, surface analysis techniques. These techniques provide complimentary information regarding both the composition and microstructure of the surface of a sample and often compliments bulk analysis.

In my talk, I will discuss the characterization challenges faced in an industrial setting where the surface analyst is often provided non-ideal samples and is asked to provide both a rapid and complete analysis of the sample. The criticality of talking with the person that submits the sample to understand their issue(s) and what they expect from the analysis (as well as being certain they realize possible complications) will be highlighted via real samples. I will also show a few examples where proof of principle results provided interesting data, however the data were not scientifically meaningful.

5:40pm **AS+TF-TuA11 C 1s Peak of Adventitious Carbon Aligns to the Vacuum Level: Dire Consequences for Material's Bonding Assignment by Photoelectron Spectroscopy**, ***Grzegorz Greczynski***, *L. Hultman*, Linköping University, Sweden

X-ray photoelectron spectroscopy (XPS) is an irreplaceable analytical tool in materials research providing information about surface chemistry and composition. The unambiguous bonding assignment relies, however, on the correct measurement of binding energy (BE) values, which is often a nontrivial task due to the lack of an internal BE reference. C 1s signal from ubiquitous carbon contamination on samples forming during air exposure, so called adventitious carbon (AdC) layers, is the most common BE reference in XPS studies. Our literature review shows that in 58% of the top-cited papers dealing with XPS studies of magnetron sputtered films published between 2010 and 2016 in peer-reviewed journals, C 1s of AdC was used as a BE reference, while, alarmingly, the remaining papers lack information about any referencing method used. Within the first group, C 1s peak was set quite arbitrary at the BE varying from 284.0 to 285.2 eV. This serious inconsistency contradicts the very notion of a BE reference, which per definition should be connected with one single-energy value.

In this work, we examine the reliability of using AdC for XPS BE referencing by measuring the position of C 1s peak for a series of transition metal (TM) nitride thin film layers that exhibit a well-defined Fermi edge cut-off serving as an internal BE reference. Measurements are performed as a function of the AdC layer thickness, which scales with the air exposure time. We show that the BE of C 1s peak E^F_B varies by as much as 1.44 eV, depending on the underlying (TM)N.[i] This is a factor of ten more than the typical resolvable difference between two chemical states of the same element, *which makes BE referencing against the C 1s peak unreliable and thus inadvisable for the purpose*. Surprisingly and reassuringly, we find that C 1s shifts correlate to changes in sample work function Φ_{SA}, such that the sum $E^F_B+\Phi_{SA}$ is constant at 289.50±0.15 eV, irrespective of materials system and air exposure time, indicating vacuum level alignment. This discovery allows for significantly better accuracy of chemical state determination through a complementary measurement of Φ_{SA} and referencing to C 1s set at $289.50-\Phi_{SA}$, which as we demonstrate, yields consistent results for the whole series of TM nitrides, irrespective of air exposure time. Our findings are not specific to nitrides and likely apply to all systems where charge transfer at the AdC/substrate interface is negligible.

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6:00pm **AS+TF-TuA12 Band Energy Alignment Studies at Heterojunction by X-ray Photoelectron Spectroscopy (XPS)**, ***Jisheng Pan***, Institute of Materials Research and Engineering, A*STAR (Agency for Science, Technology and Research), Singapore

The performance of any type of hetero-junction device is determined by two kinds of interface parameters: the band discontinuities and the built-in potential. Therefore, determining heterojunction band offsets and tuning them to a desired application would have an obvious impact on the optimization of the devices. Many techniques have been developed to determine the interfaces and to understand the microscopic origin of the interface properties. XPS is more widely used technique to study band alignment of heterojunction, probably due to its capability to simultaneously detect interface chemical and electronic properties which can be exploited for fully understanding of distinct correlations between the thin film material characteristics and device performance. There are two ways to obtain energy band offsets using XPS. One is direct measurement of valence band spectrum from interface, and this spectrum is simply considered as a superposition of substrate-related and overlayer-related valence band spectra. A nonlinear least squares fit is performed to separate it to substrate-related and overlayer-related valence band spectra to determine two valence band maxima and, valence band offset (VBO) of interface. The conduction-band offset CBO is deduced from VBO and suitable reference gap values of two materials at interface. It can be seen that the accuracy of the band offsets determined through this way depends on the fitting procedure. In order to overcome the above problem and obtain reliable band offset data, a method was proposed to determinate band offsets by combination of core level and valence band spectra. No fitting procedure is involved in this method. However, accurate XPS determination of band alignment in this way requires careful consideration of many other possible effects. In this paper, we have studied the effects of chemical shift, differential charging, band bending and photoemission final state on the determination of heterojunction band offsets using Kraut's method. The method has also been applied to determinate energy-band alignments of molybdenum disulphide (MoS_2) monolayer on high-k dielectric oxides such as Al_2O_3 and ZrO_2. The VBO at monolayer MoS_2/Al_2O_3 (ZrO_2) interface was measured to be 3.31 eV (2.76 eV), while the CBO was 3.56 eV (1.22 eV). For bulk MoS_2/Al_2O_3 interface, both VBO and CBO increase by 0.3 eV, due to the upwards shift of Mo $4dz^2$ band. The symmetric change of VBO and CBO implies Fermi level pinning by interfacial states. Our finding ensures the practical application of both p-type and n-type MoS_2 based complementary metal-oxide semiconductor and other transistor devices using Al_2O_3 and ZrO_2 as gate materials.

Biomaterial Interfaces Division
Room: 12 - Session BI+AS+MI+SA-TuA

Bio from 2D to 3D: Challenges in Fabrication and Characterization & Flash Presentations

Moderators: Lara Gamble, University of Washington, Anna Belu, Medtronic

2:20pm **BI+AS+MI+SA-TuA1 Cell-instructive Polymer Matrices for Therapies and Tissue Models**, ***Carsten Werner***, Leibniz Institute of Polymer Research Dresden and TU Dresden, Deutschland **INVITED**

Sulphated and non-sulphated glycosaminoglycans (GAGs) can be instrumental in biomedical technologies beyond. In particular, incorporation of GAGs into biomaterials has been demonstrated to allow for the biomimetic modulation of growth factor signaling, providing control over therapeutically relevant cell fate decisions in various different settings. In an attempt to systematically explore the related options, we have introduced a rational design strategy for biology-inspired hydrogels based on multi-armed poly(ethylene glycol), GAGs and peptides (1,2,3). The theoretically predicted decoupling of biochemical and mechanical gel properties was confirmed experimentally and applied for implementing GAG-based biofunctionalization schemes to afford cell adhesiveness and morphogen presentation. A number of applications of customized GAG-based materials will be given, including inflammation-modulating wound dressings (3), cryogel particles to support cell replacement in Parkinson's disease (4) and gel matrices to enable tissue and disease *in vitro* models for cancer biology (5,6) and nephrotoxicity studies. In sum, our reported approach demonstrates the power of joint theoretical and experimental efforts in creating bioactive materials with specifically and independently controllable characteristics (7).

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3:00pm **BI+AS+MI+SA-TuA3 Plant Virus Particles for 2D and 3D Architectures on Surfaces**, *V. Rink*, University of Kaiserslautern, Germany, *M. Braun*, RLP Agroscience GmbH, Germany, *M. Ani*, University of Kaiserslautern, Germany, *K. Boonrood*, RLP Agroscience GmbH, Germany, *C. Müller-Renno*, University of Kaiserslautern, Germany, *G. Krczal-Gehring*, RLP Agroscience GmbH, Germany, ***Christiane Ziegler***, University of Kaiserslautern, Germany

Biohybrid materials consist of biological entities and artificial, often inorganic materials. These biohybrids may be used in many fields of applications, ranging from biosensors to implant materials. In this context, bottom-up approaches, in which small elementary building blocks of matter are used to form larger elements through self-assembly have gained a lot of interest.

Plant viruses are promising candidates for such building blocks. Because of their simple structure and pre-defined size and form they have a high potential for self-assembly. Furthermore they can be genetically manipulated to create new functionalities by extending the capsid with different side chains.

We could show that unspecific electrostatic interactions govern the formation of large ordered 2D structures of self-assembled icosahedral tomato bushy stunt virus (TBSV) particles. By adding amino acid side chains to the capsid subunit the isoelectric point of the virus is changed. Thus by the right combination of virus modification, substrate and pH (and as a minor effect ionic strength) one can control the dimensions of 2D virus islands which may form layers with macroscopic dimensions. Specific structures in these 2D layers may be introduced by substrates which are pre-structured, e.g. by nano imprint lithography.

In addition to the electrostatic control the amino acid side chains allow also more specific interactions. Examples are histidine side chains interacting with Ni ions or gold binding peptide side chains with Au. With these specific interactions, also the third dimension is accessible. This opens the possibility to play with viruses in a kind of nano Lego which will soon become reality.

In this contribution we will show a scanning force and scanning electron microscopy study of the self-assembly of 2D and 3D structures of TBSV on Si and mica surfaces. The three dimensional structure is based on a homogeneous layer consisting of virus-particles carrying additional 4xAsp6xHis side chains (lowest stack). For the following second stack the chemical selectivity of these side chains to Ni ions (here: Ni-nitrilotriacetic acid (Ni-NTA) carrying a 5 nm Au nanoparticle was utilized. Au-binding virus-particles interact with these Au particles and create the third stack of this 3D virus architecture. The success of this strategy could be proven by SFM height measurements which reveal a height in the range of 66 nm, which corresponds to two layers of virus particles (30 nm each) coupled by Ni-NTA.

Lüders et al. (2012). Tomato bushy stunt viruses (TBSV) in nanotechnology investigated by scanning force and scanning electron microscopy. *Colloids Surf. B91*, 154

3:20pm **BI+AS+MI+SA-TuA4 Designing Thermo-responsive Nanocomposites that Provides Multiple Defense Mechanisms against Fouling**, ***Ya Liu***, University of Pittsburgh, *C. Zhang, S. Kolle, J. Aizenberg*, Harvard University, *A.C. Balazs*, University of Pittsburgh

We use computational modeling to design synthetic gel-based composite coatings that provide multiple defense mechanism against the fouling of the underlying substrate. The system encompasses rigid posts embedded in a lower critical solution temperature (LCST) thermo-responsive gel, which swells at lower temperatures and collapses at higher temperatures. By developing new dissipative particle dynamics (DPD) simulationd that capture the cell-surface interactions , we exam the biofilm growth and structure development on the substrates and pinpoint the parameter space that yields the optimal antifouling behavior for this system. The advantage of our approach relies on physical mechanisms and doesn't have unwanted environmental consequences.

4:20pm **BI+AS+MI+SA-TuA7 3D Ink-jet Printing for Tissue Engineering**, ***Thomas Boland***, The University of Texas at El Paso **INVITED**

An inkjet application is described, where biologically active ink, which may include drugs and living cells as well as non-active can be deposited alongside scaffolding materials to build two- and three-dimensional constructs for medical treatment. The technology faces several limitations that present interesting engineering opportunities. The nature and scope of the problems will be discussed in the context of the fabrication of microvasculature. The current tissue engineering paradigm is that successfully engineered thick tissues must include vasculature. As biological approaches alone such as growth factors have fallen short of their promises, one may look for an engineering approach to build microvasculature. Layer-by-layer approaches for customized fabrication of cell/scaffold constructs have shown some potential in building complex 3D structures and with the advent of cell printing, one may be able to build precise human microvasculature. Several research projects will be presented. The fabrication of microvsculatures for skin and adipose tissue engineering and current studies to characterize the biology and functionality of these engineered structures will be presented. These data suggests that a combined simultaneous cell and scaffold printing can promote microvasculature formation and improve current tissue engineering technology.

5:00pm **BI+AS+MI+SA-TuA9 Digging for Answers: Challenges in ToF-SIMS Tissue Depth Profiling**, ***Daniel Graham***, *T.B. Angerer, L.J. Gamble*, University of Washington, Seattle

The advent of cluster ion beams for time-of-flight secondary ion mass spectrometry (ToF-SIMS) instrumentation has opened up many opportunities for depth profiling organic samples. Combined with its high lateral resolution imaging capabilities, SIMS can provide 3D imaging information from a wide range of organic materials including cells and tissues. The ability to track chemical changes both across and throughout tissue sections could help identify molecular changes related to targeted drug delivery or disease states in the cellular micro-environment. While there have been many studies showing the utility of ToF-SIMS depth profiling for polymer materials, similar studies with cells and tissues have been limited. This has likely been due to the challenges encountered when working with biological samples. It has been shown that one can depth profile cells as long as the levels of buffer salts and other inorganic components is minimized. Similar work with depth profiling tissues has been limited. Herein we will present our findings on the challenges of depth profiling tissues and discuss ways these challenges may be avoided. Examples will be shown using both single beam argon cluster depth profiling and dual beam depth profiling using Bi3+ for analysis and argon clusters for sputtering. In general a significant loss in signal is seen after the first few layers of a tissue depth profile. This could be due to migration of components to the surface, ion beam damage, or ion suppression due to salts. In spite of these issues, tissue depth profiles can be acquired in most cases. The challenge then becomes processing and interpreting these large data sets. Ideas on how to overcome these challenges will be presented.

5:20pm **BI+AS+MI+SA-TuA10 Cryo-SIMS – Metrology of Biological Sample Preparation Methods for Preservation of Cell Ultrastructure and Chemistry**, ***Paulina Rakowska***, *J.-L. Vorng, I.S. Gilmore*, National Physical Laboratory, UK

With the potential of high-throughput, high-resolution and high-sensitivity label-free imaging in 3D, secondary ion mass spectrometry imaging methods are, arguably, ones of the most powerful techniques for high-resolution chemical imaging of biological samples. However, there are some critical limitations for these analyses. As the high-performance SIMS instruments require high vacuum, a careful consideration of sample preparations is often needed. For example, advanced methods are necessary to prepare and measure complex hydrated bacterial biofilm structures. Also, in the pharmacological imaging of potential drug candidates at their targets, the positioning of water soluble drug compounds within cells or tissues can be altered by pre-treatment processes such as drying, resin-embedding or histological fixation. Advanced cryo-preparation methods are necessary for immobilisation of water in these samples to prevent the ultrastructural reorganisation and the loss or translocation of water-soluble molecules, to circumvent the use of chemical fixation and to enable their analysis in high-vacuum of mass spectrometry instruments.

The UK’s National Centre of Excellence in Mass Spectrometry Imaging (NiCE MSI) at NPL has a special focus on the development of advanced solutions to challenging measurements. Our recently innovated 3D OrbiSIMS instrument has the capability to handle and measure cryogenically-prepared samples. The instrument is equipped with a vacuum cryo transfer system that is compatible with cryo-SEM and cryo-TEM. A shuttle chamber allows the interchange of samples, in vacuum and cryogenically, between cryo-preparative equipment and the 3D OrbiSIMS instrument.

This presentation will show our recent developments of the cryo-SIMS methodologies. Different sample cryo-preparation techniques will be compared, such as the analysis performed on frozen-hydrated vs. frozen-dehydrated mammalian cells. The application of cryo-SIMS to a range of biological samples including cells, bacteria, biofilms and organic reference samples will be presented. Focus will be given to the use of different types of cryo-protectants, often required for the vitrification of thicker samples such as biofilms, by high-pressure freezing and their effects on SIMS analysis.

5:40pm **BI+AS+MI+SA-TuA11 Towards Cryogenic 3D Nano-XRF Imaging of Biological Samples**, ***Axel Rosenhahn***, *S. Stuhr, C. Rumancev, T. Senkbeil, T. Gorniak, A. von Gundlach, J. Reinhardt*, Ruhr-University Bochum, Germany, *Y. Yang, P. Cloetens,* ESRF, France, *M. Grunze,* Karlsruhe Institute of Technology (KIT), Germany, *J. Garrevoet, G. Falkenberg, W. Schröder,* DESY, Germany

Nanoprobe X-ray fluorescence (nano-XRF) analysis allows spatially resolved imaging with chemical sensitivity. Approaching the diffraction limit at the next generation of storage rings, both, spatial resolution and brilliance are going to be strongly enhanced for nano-XRF experiments. For biological samples, the combination of nano-XRF with cryogenic sample environments allows to understand elemental distributions in cells with minimum preparation artefacts. In addition, the cryo-protected samples provide enhanced resistance against radiation damage, which is particularly important for the high photon densities at modern synchrotron sources. Three different applications of cryo-nano-XRF will be presented. For single melanosomes, the technique enabled us to prove the core-shell organization of the organelles using metals as surrogate markers. As second application, the distribution of metals in single, adherent cells was directly imaged without the requirement of additional markers. Finally, marine adhesives of diatoms were analyzed and the occurrence of metals are linked with the known organic constituents in the EPS of diatoms. In all three cases, the detection of metal distribution has provided a new view on the investigated samples. The cryogenic sample environments proved to be the key to apply synchrotron radiation to all three types of biological samples. The data will also be discussed in relation to the perspectives of new implementations that will enable fast cryo-3D imaging in the future.

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic
Room: 9 - Session SA+AS+HC+SS-TuA

Frontiers of Photoelectron Spectroscopy: Surface & Interface Processes with Variable Depth Probe, High Spatial or Temporal Resolution
Moderators: Geoff Thornton, University College London, Carla Bittencourt, University of Mons, Belgium

2:20pm **SA+AS+HC+SS-TuA1 AVS 2017 Medard W. Welch Award Lecture: Ionic Liquid Surface Science**, ***Hans-Peter Steinrück****, University Erlangen-Nuernberg, Germany **INVITED**

Ionic liquids (ILs) are molten salts with a melting point below 100∘C. They represent a new class of liquid materials with unique property profiles originating from a complex interplay of Coulombic, hydrogen bonding, and van der Waals interactions of their ions. The enormous variety of cation-anion combinations enables tuning of the physico-chemical properties over a wide range. Functional groups can be implemented in their chemical structure to adapt them for specific tasks - such functionalized ILs are known as ’task-specific ionic liquids’. Applications range from catalysis and organic synthesis to tribology, protective coatings and gate dielectrics. In catalysis, two important concepts are Supported Ionic Liquid Phase (SILP) and Solid Catalyst with Ionic Liquid Layer (SCILL). In both, a high surface area solid substrate is covered with a thin IL film, which contains either a homogeneously dissolved transition metal complex for SILP, or which modifies catalytically active surface sites at the support for SCILL. The interface of the IL with the gas phase/vacuum or with the solid support plays an important role. Therefore, knowledge about surface and interface properties and their relation to the chemical structure is of pivotal importance for choosing the right IL for a specific application. In contrast to most other liquids, ionic liquids have a very low vapor pressure, and thus can be studied with the methods of ultrahigh vacuum-based surface science. One particularly powerful method is angle-resolved X-ray photoelectron spectroscopy. Thereby, detailed information on their surface composition, on segregation and enrichment effects, on the dissolution and reactivity of catalytically active metal complexes, on the growth of ultrathin IL-layers, and even on reactions in the liquid phase, can be obtained. Several examples will be discussed illustrating the power of surface science to study this new materials class. Many of the derived conclusions are considered representative for liquid surfaces in general.

F. Maier, I. Niedermaier, and H.-P. Steinrück, *"Perspective: Chemical Reactions in Ionic Liquids Monitored through the Gas (Vacuum)/Liquid Interface"*, J.Chem. Phys. **2017** (in press)

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

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

H.-P. Steinrück, "*Surface Science goes liquid !*", Surf. Sci. **2010**, *604*, 481.

3:00pm **SA+AS+HC+SS-TuA3 *In Situ* Characterization of Semiconductor Nanowire Devices by Nano-Focus X-ray Photoemission Microscopy and Spectroscopy**, *S. McKibbin,* ***Andrea Troian***, *S. Yngman,* Lund University, Sweden, *H. Sezen, M. Amati, L. Gregoratti,* Elettra-Sincrotrone Trieste, Italy, *A. Mikkelsen, R. Timm,* Lund University, Sweden

III-V semiconductor nanowires (NWs) have a large technological potential within electronics, optoelectronics, and energy harvesting [1,2], mainly due to their flexibility in creating heterostructures by axial stacking during epitaxial growth. Because of their small diameter and their very large surface-to-volume-ratio, the performance of NW devices is strongly determined by surface properties. X-ray photoemission spectroscopy (XPS) has been proven highly suitable for studying surface composition and electronic properties of homogeneous NWs [3]. However, in order to better understand NW device performance, it is essential to also investigate NW heterostructures, with nm-scale lateral resolution and during device operation.

Here, we will present nano-focus XPS results from material and doping heterostructures in InP and GaInP NWs intended for photovoltaic application [2]. We used scanning photoemission microscopy (SPEM) at the ESCAMicroscopy beamline of the ELETTRA synchrotron, providing a lateral resolution of about 120 nm, for imaging individual NWs. In addition, we revealed the change in local surface potential across (Ga)InP *pn*-junctions and InP/GaP tunnel junctions, obtained from In 3d, In 4d, and P 2p XP spectra

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* **Medard W. Welch Award Winner**

acquired along the heterostructure NW. Electrical contacts were provided to both ends of the investigated NW, allowing to vary the source-drain bias along the NW during SPEM characterization. We will present detailed results on the influence of built-in potential and external forward and backward bias on the surface potential distribution across NW interfaces.

In another approach, we aim at revealing *in-situ* the interplay of surface chemical composition and local electronic properties. As a model system, we chose InAs NWs consisting of several segments of wurtzite and zincblende crystal structure [4]. At the interface between such segments, we confirmed a staggered type-II electronic band alignment, obtained from nano-focus XP spectra along externally biased NWs. After removing the native oxide from the NW surface by atomic hydrogen annealing [4] in the XPS UHV chamber, the same NW instead showed flat-band conditions, which is preferential for electronic application [1]. We will discuss future plans of using the dynamic high pressure option of the ESCAMicroscopy beamline for changing the surface chemistry of NWs while simultaneously investigating them with SPEM and nm-scale spectroscopy.

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3:20pm **SA+AS+HC+SS-TuA4 Introducing Ionic-Current Detection for X-ray Absorption Spectroscopy in Liquid Cells**, ***Daniela Schoen***, Helmholtz-Zentrum Berlin, Germany

Photons and electrons are two common relaxation products upon X-ray absorption, enabling fluorescence yield and electron yield detections for X-ray absorption spectroscopy (XAS). The ions that are created during the electron yield process are relaxation products too, which are exploited in this study to produce ion yield for XA detection. The ionic currents measured in a liquid cell filled with water or iron(III) nitrate aqueous solutions exhibit characteristic O K-edge and Fe L-edge absorption profiles as a function of excitation energy. Application of two electrodes installed in the cell is crucial for obtaining the XA spectra of the liquids behind the membrane. Using a single electrode can only probe the species adsorbed on the membrane surface. The ionic-current detection, termed as total ion yield (TIY) in this study, also produces an undistorted Fe L-edge XA spectrum, indicating its promising role as a novel detection method for XAS in liquid cell.

5:00pm **SA+AS+HC+SS-TuA9 Non-destructive Depth Profiling of $LaAlO_3/SrTiO_3$ Interfaces**, ***Conan Weiland***, NIST, *A.K. Rumaiz,* National Synchrotron Light Source II, Brookhaven National Laboratory, *G.E. Sterbinsky*, Advanced Photon Source, Argonne National Laboratory*, J.C. Woicik*, NIST

The interface between $LaAlO_3$ (LAO) and $SrTiO_3$ (STO) is known to be conductive, even though both LAO and STO are insulators. The interface may also host a variety of interesting phenomena such as a two-dimensional electron gas, ferromagnetism, and superconductivity. Various mechanisms have been proposed to explain the formation of the conductive interface, including the 'polar catastrophe', wherein the polar discontinuity at the interface leads to a diverging potential allowing electronic reconstruction, oxygen vacancies at the interface or at the LAO surface, and chemical intermixing, amongst others.

Synchrotron-based variable kinetic energy x-ray photoelectron spectroscopy (VKE-XPS) is a unique and powerful tool to non-destructively probe the chemical and electronic structure of buried interfaces such as that between LAO and STO. Using VKE-XPS, we have analyzed a series of LAO films on STO and have observed compositional variations in the LAO films as a function of depth: Al-enrichment occurs at the LAO surface. Additionally, an electric field was observed in some samples. In this presentation we will discuss the relevance of these results on the formation of conductive LAO/STO interfaces.

5:20pm **SA+AS+HC+SS-TuA10 Hard X-ray Photoelectron Spectroscopy Study of the Resistive Switching in Te-based Conductive Bridging Random Access Memories**, ***Munique Kazar Mendes***, *E. Martinez, O.J. Renault, R. Gassilloud, M. Bernard, M. Veillerot,* CEA/LETI-University Grenoble Alpes, France*, J.M. Ablett,* Synchrotron SOLEIL, France, *N. Barrett*, SPEC, CEA Saclay - University Paris-Saclay, France

Conductive bridging random access memories (CBRAM) are emerging devices for the next generation of non-volatile memories (NVM) (1). The CBRAM mechanism is related to ionic transport and electrochemical reactions, which give rise to the formation and dissolution of a conductive filament through the insulating dielectric layer (2). Data storage relies on switching the resistivity between two high (HRS) and low (LRS) resistance states by applying voltage or current pulses. We investigate the electrochemical reactions involved in the switching mechanism of Al_2O_3-based CBRAMs with different active electrodes (TiTe and ZrTe) (3). We have used hard X-ray photoelectron spectroscopy to learn about electrochemical reactions involved in the switching mechanism with sufficient depth sensitivity. Photon energies of 6.9, 8.0 and 10.0 keV were chosen to obtain a non-destructive in-depth chemical characterization with varying sampling depths. The HAXPES experiments were performed at the Galaxies beamline (Soleil) on As-grown samples, after ex-situ forming (Formed) and after Reset operations. The comparison between these different resistance states shows the role and evolution of the electrode/electrolyte interfaces during electrical biasing. For the $TaN/TiTe/Al_2O_3/Ta$ stack, results highlight, the reduction of Ti together with alumina oxidation after forming. The sample polarization causes oxygen migration, probably in the O^{2-} form, pushed by the upper negative bias towards the interface between the active electrode and the solid electrolyte (Al_2O_3). When reversing the polarity of the applied voltage (Reset operation), we observe Ti reoxidation and alumina reduction, characterizing oxygen migration towards the active TiTe electrode. These results reveal the important role of oxygen migration in the filament formation/dissolution. ToF-SIMS measurements are also performed to get complementary in-depth chemical information. We will finally compare the two active electrodes to investigate the influence of the composition on the switching mechanism.

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5:40pm **SA+AS+HC+SS-TuA11 Correlation of the Magnetic and Magnetotransport Properties, Electronic and Atomic Structure of Strongly Correlated Complex-oxide Thin Films with the Oxygen Vacancies and Films Thickness**, ***German Rafael Castro***, Spanish CRG BM25 Beamline at the ESRF, France, *J. Rubio Zuazo*, SpLine Spanish CRG BM25 Beamline at the ESRF, France

Herewith, we present structural, electronic, morphological and magnetotransport properties of thin films of perovskite-manganese oxides (maganites) grown on SrTiO3(001) by oxygen assisted pulsed laser deposition (PLD) methods, using Hard X-ray Photoelectron Spectroscopy (HAXPES), and Grazing Incidence X-ray diffraction (GIXRD).

Perovskite-manganese oxides exhibit a wide variety of interesting physical properties which originate from mutual coupling among spin, charge and lattice degrees of freedom. $La_{1-X}CaxMnO_3$–type perovskite-manganese oxides are strongly correlated electron systems and exhibit, in the Ca doping range between 0.15 and 0.5, a ferromagnetic–paramagnetic (FM) phase transition accompanied by a metal–insulator (MI) transition that results in a colossal magneto-resistance behaviour. In bulk $La_{0.7}Ca_{0.3}MnO_3$ (LCMO), the transition temperature TFM, TMI rises for 33% Ca doping level reaching values close to room temperature. The results shown here are focused on the study of the influence of buried interfaces and the oxygen vacancies on the electric and magnetotransport properties of $La_{0.7}Ca_{0.3}MnO_3$ thin films grown on $SrTiO_3(001)$

The growth of these materials in thin film form opens possibilities for magneto-electronic devices applications. The atomic and electronic structures, as well as the oxygen content, are followed simultaneously by GIXRD and HAXPES. Combining GIXRD, HAXPES and transport techniques, we have established a correlation between the electronic, atomic structure and magnetic and magnetotransport properties of $La_{0.7}Ca_{0.3}MnO_3$ thin films as a function of the oxygen vacancies and films thickness.

6:00pm **SA+AS+HC+SS-TuA12 Synchrotron–Based X-ray Spectroscopy Studies of Inorganic-Organic Hybrid Halide Perovskite Materials Surfaces and Properties**, ***Deidra Hodges***, *S. Shahriar, A.K. Mishra, V. Castaneda, V. Vidal, M. Martinez, N. Garcia, J. Munoz, J. Lopez*, University of Texas at El Paso

Recently, the methylammonium lead iodide $CH_3NH_3PbI_3$ perovskites have attracted a lot of attention as a possible absorber material for thin film solar cells due to their bandgap energy, high optical absorption coefficients and low-cost solution-processing deposition approaches. Methylammonium lead iodide $CH_3NH_3PbI_3$ perovskite solar cells have evolved with transformative potential with laboratory efficiencies greater than 20%. Perovskite absorber materials are very inexpensive to synthesize and simple to manufacture, making them an extremely commercially viable option. Solar cell efficiencies of devices using these materials have increased from 3.8% in 2009 to a Newport certified 20.1% in 2015, making this the fastest-advancing solar cell technology to date. These devices are known for their high photon absorptivity, tunable large direct band gaps with superior carrier charge transports, and low-cost methods of fabrication. Methylammonium lead tri-iodide $CH_3NH_3PbI_3$ perovskites thin films and single crystals were prepared for synchrotron-based X-ray spectroscopy studies of the perovskite materials surfaces and properties. The perovskite thin films and single crystals were characterized at the National Synchrotron Light Source (II) (NSLS-II) at Brookhaven National Laboratory (BNL). Synchrotron-radiation-based chemical analysis using X-ray fluorescence (XRF), and X-ray absorption near edge structure (XANES) spectroscopy were performed on samples for detailed analysis into chemical composition, stoichiometry, and material surface properties.

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

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

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

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

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

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

[+] Author for correspondence: omur.dagdeviren@yale.edu

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

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

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

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

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

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

These three samples were scanned on $1.5 \times 1.5 \mu m^2$ square area with a resolution of 30x30 pixels and analyzed using the proposed local DLTS method.

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

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

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

*** NSTD Student Award Finalist**

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Beyond Traditional Surface Analysis: Pushing the Limits

Moderators: Svitlana Pylypenko, Colorado School of Mines, Paul Vlasak, The Dow Chemical Company

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

[1] S. Ninomiya, K. Ichiki, H. Yamada, Y. Nakata, T. Seki, T. Aoki, J. Matsuo, Rapid Commun. Mass Spectrom. 23, 2009, 1601.

[2] M. P. Seah, The Journal of Physical Chemistry C 117(24), 2013, 12622.

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

In 1987 Appelhans and co-workers performed a groundbreaking experiment. They bombarded a polymer surface with a neutral SF6 beam in order to avoid charging effects on insulators. By coincidence they discovered that "the SF_6 beam is doing an excellent job of producing secondary ions ... it is unexpectedly efficient at sputtering secondary ions from these polymer surfaces "[1].

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

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

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

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

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

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[2] M. Benguerba, et. al. Nucl. Instrum. Meth. B 62 (1991) pp. 8-22.

[3] Kollmer, F. (2004): Applied Surface Science 231-232, pp. 153–158

[4] Kollmer, F. et. al. (2013) Surface and Interface Analysis 45 (1), pp. 312–314

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

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

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

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3) J. Brison and L. Houssiau, *Surf. Interface Anal*. 2006; 38: 1715-1719.

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

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

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*** ASSD Peter Sherwood Award**

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Sustainability Focus Topic
Room: 5 & 6 - Session SU+AS+EM+MS-WeM

Piezoelectrics, Thermoelectrics, and Superconductors

Moderators: George Nolas, University of South Florida, Kimberly Cook-Chennault, Rutgers University

8:20am **SU+AS+EM+MS-WeM2 Investigation into Novel p-type Thermoelectric Materials**, ***Dean Hobbis***, *K. Wei, G.S. Nolas*, University of South Florida

Novel thermoelectric materials are in high demand due to the ability to directly convert waste heat into electrical power, a process that has limitless applications both privately and commercially. Currently n-type thermoelectric materials have been more vastly studied than p-type and have been optimized to higher Figures of Merit (ZT). A thermoelectric module requires both n-type and p-type materials, therefore the efficiency of the module is characterized by the combination of ZT values. This means the optimization of p-type thermoelectric materials is extremely important to the commercial viability of thermoelectric technology. Furthermore, the particular synthesis method is also of importance for applications in industry. In skutterudites, for example, methods of fractional filling are typically used to improve thermoelectric efficiency by promoting phonon scattering to reduce thermal conductivity in the material, but most of the elements used as filler are electron donors. Nevertheless, Br is an electron acceptor when used as a filling atom [1]. In quaternary chalcogenides, thermal conductivity can be intrinsically low due to the crystal structure so methods to improve electrical transport is often employed through alloying and substitution on different atomic sites. Certain antimonides also possess intrinsically low thermal conductivity. Furthermore, differing processing conditions can influence the transport properties significantly, resulting in different ZT values. In this talk we present our latest work on these material systems, including new data that shows substantial improvement In ZT with composition and processing conditions.

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8:40am **SU+AS+EM+MS-WeM3 Thermoelectrics for Sustainable Energy Harvesting**, ***Mary Anne White***, Dalhousie University, Canada **INVITED**

Thermoelectrics can convert heat to power. The key to this process is the combined electrical (high electrical conductivity and Seebeck coefficient) and thermal (low thermal conductivity) properties. Although thermoelectrics have been used commercially for more than 50 years, new materials with higher efficiency could make their use more widespread. A large fraction of energy consumed is actually wasted as heat, so efficient conversion of this waste heat to useable power would be a great advantage to humanity. After a general introduction to thermoelectrics, this presentation will focus on improvement of thermoelectrics via sustainable approaches, including consideration of sustainability of the elements, and recent work focusing on elements with high availability.

9:20am **SU+AS+EM+MS-WeM5 Toward a Greener World: The (Re)search for Lead-Free Piezoelectrics**, ***Xiaoli Tan***, Iowa State University **INVITED**

Piezoelectricity refers to the linear coupling, in the direct effect, between mechanical stress and electric displacement, and in the converse effect, between mechanical strain and applied electric field. The proportionality constants are the piezoelectric coefficients which are equivalent between the direct and the converse effects. For the past six decades ceramics based on $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) perovskite oxides have been the workhorse of piezoelectric technology due to their excellent properties, ease of processing, and low cost. The high piezoelectric performance of PZT is primarily resulted from the intrinsic lattice distortion and the ferroelectric domain switching. However, environmental concerns with lead have stimulated worldwide intensive efforts in the search for lead-free piezoelectric ceramics.

The research efforts on lead-free piezoelectric ceramics have been largely concentrated on three solid solution families: $BaTiO_3$-based, $(K_{0.5}Na_{0.5})NbO_3$-based, and $(Bi_{1/2}Na_{1/2})TiO_3$-based compositions. $BaTiO_3$-based ceramics exhibit excellent piezoelectric coefficients, but their applications are limited by their low Curie points (~100 ºC). $(K_{0.5}Na_{0.5})NbO_3$-based compositions possess high piezoelectric coefficients and relatively high Curie points (> 200 ºC), but have stringent requirements on the processing conditions. $(Bi_{1/2}Na_{1/2})TiO_3$-based polycrystalline ceramics develop giant electrostrains (up to 0.70%), but usually require a very high electric field.

In this presentation, an overview of the recent development in the search and research on lead-free piezoelectric ceramics will be given. Their chemical compositions, structure evolutions, and mechanisms for property optimization will be discussed. In addition, two specific investigations will be presented. The first one is on the microstructural response to poling electric fields in the $(Bi_{1/2}Na_{1/2})TiO_3$–$BaTiO_3$ solid solution. With the *in situ* transmission electron microscopy technique, it is directly observed that poling fields can either destroy or create morphotropic phase boundaries and the associated strong piezoelectric property. The second investigation is on the development of a giant electrostrain of 0.70% at 50 kV/cm at room temperature in $\{[Bi_{1/2}(Na_{0.84}K_{0.16})_{1/2}]_{0.96}Sr_{0.04}\}(Ti_{0.975}Nb_{0.025})O_3$. This polycrystalline ceramic with randomly oriented grains is even better than some single crystals in terms of some electromechanical properties. *In situ* transmission electron microscopy examination indicates that the giant electrostrain is originated from the reversible phase transitions under applied electric fields.

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11:20am **SU+AS+EM+MS-WeM11 Thermal Annealing Effects on the Thermoelectric Properties of Si/Si+Sb Thin Films**, ***Satilmis Budak***, *Z. Xiao, M. Curley, M. Howard, B. Rodgers, M. Alim*, Alabama A&M University

Thermoelectric devices were prepared from multi-nanolayered Si/Si+Sbthin films using DC/RF magnetron sputtering system. Thermoelectric devices were annealed at different temperatures to form quantum (nano) structures in the multilayer thin films to increase the Seebeck coefficients and electrical conductivity and decrease thermal conductivity. The prepared devices were characterized using Seebeck coefficient measurement; four probe van der Pauw measurement resistivity and the laser thermal conductivity systems. The surface morphology of the fabricated thermoelectric films is characterized using Scanning Electron Microscope (SEM+EDS).

Acknowledgement

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

11:40am **SU+AS+EM+MS-WeM12 Critical Current by Design**, ***George Crabtree***, *U. Welp*, Argonne National Laboratory, *K. Kihlstrom*, University of Illinois at Chicago, *A. Koshelev*, Argonne National Laboratory, *A. Glatz*, Northern Illinois University, *I. Sadovskyy*, *W.K. Kwok*, Argonne National Laboratory **INVITED**

We introduce a new approach for rational design of superconducting critical currents, using time-dependent Ginzburg-Landau simulation to predict the critical current produced by an arbitrary mixed pinning landscape. Time dependent Ginzburg-Landau simulations automatically take into account vortex flexibility, the variation of coherence length with temperature and field, the mutual interaction of vortices and the interaction of vortices and defects. Core pinning by an arbitrary mixed pinning landscape is included by lowering the superconducting condensation energy at points, along lines and within finite nanoscale regions corresponding to specific pinning defects. We show results for several real-world cases that verify predictive ability, outline a program for unfolding the interaction of multiple pinning defects and for maximizing the critical current in targeted temperature and field ranges

Vortices in High Performance High Temperature Superconductors, W. K. Kwok et al., Reports on Progress in Physics. 79, 116501 (2016)

Toward Superconducting Critical Current by Design, Ivan A. Sadovskyy et al, Advanced Materials 28(23), 4593-4600 (2016)

This work was supported by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, as part of the Center for Emergent Superconductivity Energy Frontier Research Center and by the Scientific Discovery through Advanced Computing (SciDAC) program funded by U.S. Department of Energy, Office of Science, Advanced Scientific Computing Research and Basic Energy Science.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

The recent advent of two dimensional semi-conducting materials of the post-graphene era, such as transition-metal dichalcogenides (TMDs- such as MoS_2, WSe_2, …) has amplified the need for advanced analytical diagnostics. One of the main issues to tackle are directly related to the atomically-thin character of the samples, first concerning the low elemental concentrations and second, the invasive character of most of the characterization techniques implemented. As a photon-probe technique, XPS has a key role to play in the analysis of TMDs but highly sensitive and versatile microscopic capabilities are needed: this is because the physics of TMDs, notably the indirect-to-direct band gap transition in the monolayer limit, requires spatially-resolved information not only on the chemical composition but also on the electronic band structure. Short analysis times are required because a screening of these properties depending on processing conditions (at the material or the device level) is needed. PEEM-based instruments are the only class of XPS microscopes able to offer both type of analysis. In this presentation, we will review recent studies of 2D materials using XPEEM for chemical imaging and *k*PEEM for band structure imaging, with a particular emphasis on instrumental requirements (excitation source, transmission and detection) and post-processing of the 3D spectroscopic image data sets. The examples will range from graphene doping [1] and cleaning [2], to single layer MoS$_2$ [3-4], including also novel materials and 2D heterostructures.

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

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

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

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

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

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

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

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

References

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

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

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

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

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

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

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

Biomaterial Interfaces Division
Room: 12 - Session BI+AS-WeA

In Honor of Dave Castner's 65th Birthday: Multitechnique Bio-Surface Characterization II

Moderators: Lara Gamble, University of Washington, Daniel Graham, University of Washington

2:20pm **BI+AS-WeA1 Contributions Advancing Surface Technologies: NEXAFS, ESCA, Rhodium (and More)**, ***Buddy D. Ratner***, University of Washington, Seattle **INVITED**

The broad impact that surface science has had on so many technologies is mirrored by the contributions of Professor David Castner to many sub-fields dependent upon surface science. Dave's earliest contributions to the scientific literature were associated with the surface science of rhodium, iron and cobalt catalysts. Papers were published addressing CO hydrogenation, Fischer-Tropsch polymerization and related topics with relevance to energy consumption and chemical production. With Dave's arrival at the University of Washington in 1986, the subjects of his research shifted from catalysis to biomedical surfaces. Dave and I have always shared a common interest (maybe passion). That is, generating quality data and extracting maximum information from that data. We both had extensive experience with early HP5950 electron spectroscopy for chemical analysis (ESCA) instruments. These monochromatized instruments generated exceptionally high resolution spectra for that era, and the instruments had effective charge compensation for insulators. This allowed us to make great strides in highlighting the use of ESCA for bio-relevant surfaces and biological materials. The theme of data quality has persisted into the present with newer ESCA instruments and then SIMS instrumentation. Dave Castner has taken surface analysis into the 21st century with studies on cells, proteins, novel polymer surfaces and nano-materials. This talk will highlight Dave Castner's remarkable contributions to surface science with particular emphasis on his contributions to the evolution of methods available to analyze complex surfaces and morphologies.

3:00pm **BI+AS-WeA3 Characterization of Bio-Molecules with GCIB-SIMS equipped with MS/MS Spectrometer**, ***Jiro Matsuo***, *T. Seki, T. Aoki*, Kyoto University, SENTA, JST, Japan

Secondary ion mass spectrometry (SIMS) is now widely used for chemical analysis of polymers and biological materials that have a rather complicated molecular structure. Various types of primary ion beams and mass spectrometers have been developed and used in an attempt to improve sensitivity, as well as lateral and mass resolution. Large gas cluster ion beams (GCIB) have been commercialized for surface analysis techniques, such as SIMS and XPS. Molecular depth profiling and three-dimensional analysis have been applied on organic devices and biological materials. A large cluster ion beam could overcome the limitation of ion dose, which is the biggest obstacle for obtaining more signals in static SIMS.

To expand the applications of the SIMS technique, we have developed a finely focused large cluster ion beam (~1mm) for the primary ion beam for use in SIMS [1] and combined it with mass spectrometers of the quadrupole time-of-flight mass spectrometry (Q-TOF) type without pulsing primary ions. This mass spectrometer is equipped with MS/MS capability and allows to determine the structure of the secondary ion by using the collision-induced dissociation (CID) technique. This is a new SIMS instrument that helps in the characterization of biomolecules in cells, tissue and medicine. For instance, the detection limit of a drug molecule is improved by using the MS/MS technique, because of a much-reduced background.

In this paper, we demonstrate the capability of SIMS with the MS/MS spectrometer to determine the structure of molecular-related ions and discuss the benefits and drawbacks of this technique.

[1] J. Matsuo, S. Torii, K. Yamauchi, K. Wakamoto, M. Kusakari, S. Nakagawa, M. Fujii, T. Aoki, and T. Seki, *Appl. Phys. Express*, ***7*** (2014), 056602

3:20pm **BI+AS-WeA4 Linking Nanosilver (AgNP) Toxicity to the Physicochemical Properties of the Particles which can Change as a Function of Experimental and Biological Conditions**, ***Donald Baer***, Pacific Northwest National Laboratory, *J.M. Brown*, University of Colorado at Denver, *A. Porter*, Imperial College London, UK, *B.D. Thrall*, Pacific Northwest National Laboratory, *T.D. Tetley*, Imperial College London, UK, *L.S. Van Winkle*, University of California at Davis, *T. Xia*, University of California at Los Angeles

Although colloidal Ag is generally considered safe for humans, use of nanosilver in consumer products has dramatically increased both the amount of Ag exposure and possible exposure pathways. To fill knowledge gaps for nano-Ag safety assessment, the National Institute of Environmental Health Sciences supported a consortium of investigators to examine how physical and chemical characteristics of AgNPs can lead to adverse health outcomes. Here we report a consortium perspective linking physicochemical properties of the particles to Ag biodistribution and toxicity. It is necessary to recognize the dynamic nature of AgNPs. They can change in response to handling and variations in their environment and such changes can influence Ag biodistribution and biological responses. Consortium studies identified the critical relationships among AgNP properties, environmental effects, and the biodistribution and fate of Ag associated with the particles. Three critical regions of interactions were identified: i) effect of exposure medium and biological environment on particle properties and transformations; ii) processes occurring at the cellular surface impacting particle attachment, uptake, accumulation and clearance; and iii) particle fate and transformations within a cell. The nature of AgNPs during biological exposure is influenced by the initial characteristics of the particles including size, structure and the presence of designed or inadvertent coatings. These initial properties are usually altered by exposure to artificial or natural media. These physicochemical properties are often time dependent and such changes, including often ignored effects due to handling or storage, can influence biological outcomes. Ag can be transported into cells as both ions and particles. While ions are known to impact cytotoxicity, AgNPs within cells often have greater toxicity. Intercellular processes are similar to those in extracellular media except that the Ag is located within specific microenvironments within a cell. It appears that intracellular dissolution of Ag is a major cause of toxicity.

4:20pm **BI+AS-WeA7 Protein Imaging from the Subcellular Level to the Single Protein Level**, ***DaeWon Moon***, DGIST, Republic of Korea

Most of biological story tellings are mainly based on proteins and their interactions. Therefore protein imaging and their interaction studies have been the key interest in bio imaging. Most of protein bioimaging have been based on confocal fluorescence microscopy for 2 or 3 proteins. We have developed a new multiplex protein imaging method for TOF-SIMS with metal oxide nanoparticle (MONP) conjugated with proteins up to 9 proteins, in theory, several tens, and a single protein imaging technique based on He Ion Microscopy (HIM)

In SIMS analysis, MONPs provide high secondary ionization yield and amplification of ion yields. We systhesized 9 MONPs working right such as CoO, CdO, Fe3O4, TiO2, PbO, In2O3, SiO2, Al2O3, La2O3. In addition to protein imaging, SIMS intrinsically provides tens of bio-molecular imaging including lipids and metabolites, and metals with a TOF mass analyzer, which makes this new methodology to be an omni-molecular mass spectrometric imaging technique. Sliced and cultured mouse hippocampal tissues were imaged with typical spatial resolution of 2 µm, which can be improved down to 300 nm for 9 neuronal proteins. Proteins chosen to image mouse hippocampal tissues are NeuN for all nuclei, Cav1,3 for neuron cells, Iba1 for microglia cells, GFAP for astrocytes, AMPA receptor, phosphorylated Tau, amyloid beta (Aß) 1-42, amyloid precursor protein, and APOE, which were selected to visualize important proteins as landmarks of Alzheimer Disease (AD). With multiplex proteins imaging, we could estimate the proximity of associated proteins in mouse hippocampal tissues, which changes with aging and AD progression.

Since HIM has a spatial resolution of 0.5 nm, HIM can observe single proteins in theory but in practice, it may be very dfficult to observe a single protein molecule due to the similar secondary electron yields of proteins compared to other proteins or extracellular matrix molecules. We demonstrated that HIM can image each MONP conjugated with proteins from a mouse hippocampal tissue revealing the distribution of single proteins in synapses, neuronal soma, amyloid plaques, and neurofibrillary tangels with their changes along aging and AD.

With the co-development of multiplex protein SIMS imaging and single protein HIM imaging technology, I expect we can improve our understanding on the role of proteins and their interactions in biology, biomaterials, and medicine.

4:40pm **BI+AS-WeA8 Integrating Biological and Surface Chemical Characterisation to Probe Bacterial and Lipid Vessicle Interactions at Surfaces**, ***Sally McArthur***, Swinburne University of Technology and CSIRO, Australia, *M. Abrigo, H. Askew, K.L. Jarvis*, Swinburne University of Technology, Australia

Control and the ability to elicit specific responses from a biological system lies at the heart of most bioengineering. We want to immobilize proteins on biosensors but ask them to behave as they would in the body, stimulate cells to assemble tissues, form new blood vessels and replicate structures in the lab just as well as they can in our bodies. We want methods that prevent bacteria forming biofilms and better still we would like them to stop attaching to surfaces full stop. We have an armada of techniques at our disposal, surface engineering, macro, micro and nanomaterials, drugs and biomolecules, light, electricity and a plethora of analysis tools to give us new insight into how the systems we build behave. But as we increase the complexity of the system, we need to be able to match this with combinations of characterisation techniques that probe both the biological and physicochemical processes occurring at the biointerface.

This talk will explore how we utilise QCM, XPS, ToF-SIMS, florescence imaging and biological assays to investigate the influence of surface chemistry and micro and nanoscale topography on interactions with lipid vesicles and bacteria.

5:00pm **BI+AS-WeA9 A Physical Chemist and a Chemical Engineer Walk into a Bar… Reflections on Surface and Interface Analysis**, ***Matthew Wagner***, The Procter & Gamble Company **INVITED**

Surface and interface science is critical to many applications across many industries, spanning from advanced technologies in microelectronics and biomaterials to everyday household goods such as laundry detergents and shampoos. Micro and nanoscale phenomena at surfaces and interfaces, including adsorption, wetting, self-assembly, and many others, drive macroscale performance, resulting in significant benefits when done well and significant failures when poorly understood or controlled. At all scales, measurement science specific to surfaces and interfaces is critical to understanding these phenomena.

In the field of biomaterials science (and beyond), protein adsorption is a foundational step in all interactions between biological systems and synthetic materials. Many surface analysis techniques have been applied to the characterization of adsorbed protein films, including understanding the amount, composition, spatial distribution, and orientation of adsorbed proteins. In this special session in honor of Dave Castner, this presentation will review key contributions from the Castner group on the application of multi-technique surface analysis techniques to adsorbed protein films. In particular, the use of ToF-SIMS and multivariate data analysis techniques in conjunction with complementary surface spectroscopies including XPS, NEXAFS, SPR, and others, will be reviewed. The broader impact of these developments in surface analysis methodologies on the fields of surface and interface science across industries will be discussed.

5:40pm **BI+AS-WeA11 Investigating the Cytotoxicity of Commercially Available Poly(*N*-isopropyl Acrylamide)-coated Surfaces**, *L. Stapleton, M.A. Cooperstein, P.A.H. Nguyen,* ***Heather Canavan***, University of New Mexico

Poly (*N*-isopropyl acrylamide) (pNIPAM) is a thermoresponsive polymer that undergoes a phase change at a physiologically relevant temperature range, which leads to mammalian cell release. Below its lower critical solution temperature (LCST ~32° C), pNIPAM becomes hydrated and is hydrophilic. In this state, its chains become extended and cells detach as intact cell sheets. Before the detached cell sheets can be used on humans, the cytotoxicity of the surfaces must be accessed. In previous studies, we found that although most techniques for polymerizing NIPAM (e.g., plasma polymerization, ppNIPAM; and sol-gel preparations of NIPAM, spNIPAM) yielded biocompatible films, those from commercially available NIPAM (cpNIPAM) were relatively cytotoxic. In this work, we investigate the reasons behind this anomaly. The cpNIPAM-coated surfaces were evaluated for their thermoresponse and surface chemistry using standard surface science techniques (e.g., goniometry, X-ray photoelectron spectroscopy). The relative biocompatibility of the substrates with cultured bovine aortic endothelial cells (BAECs) and monkey kidney epithelial cells exposed to extracts from the cpNIPAM, spNIPAM, and ppNIPAM films was assessed using pop off experiments and Live/Dead assays. In addition, the extract solutions themselves were analyzed by NMR and mass spectroscopy. We find that the diminished cell viability of BAECs exposed to cpNIPAM substrates is due to a combination of factors, including the inclusion of short chain length polymers and the presence of unreacted catalyst. This work will have valuable insights into the cytotoxicity of cpNIPAM-coated surfaces, and therefore, into the applicability of cells grown on this surface for human subjects.

6:00pm **BI+AS-WeA12 Development of Surface Analysis Methods for Characterizing Immobilized Proteins**, ***David Castner***, University of Washington

One of the first events that occurs when a biomedical device is placed in the biological environment is the interactions of proteins with the surface region of the biomedical device. How the proteins interact with the surface can have a significant impact on further biological responses in both *in vivo* and *in vitro* applications. Thus, it is essential to understand how proteins interact with surfaces and any structural modifications they undergo as a result of these interactions. Key objectives for characterizing surface-bound proteins are (1) identifying the type of proteins bound to the surface, (2) determining the amount of each surface-bound protein, (3) determining the conformation and orientation of the bound proteins and (4) characterizing the spatial distributions of surface-bound proteins. There are many bonding mechanisms for attaching proteins to surfaces (charge-charge, coordination complexes, covalent bond formation, ligand interactions, etc.). Each method has its advantages and disadvantages. How the protein structure, especially its conformation and orientation, is affected by surface attachment will be a function of the surface structure and composition of the biomaterial as well as properties of the protein. There are often time-dependent changes in the composition, conformation, orientation, and distribution of the complex, multi-component protein films deposited from the biological environment. So the structural determinations for surface bound proteins need to be related not only to the properties of the biomaterial surface and protein, but also to the experimental conditions used to attach the protein to the surface. Results using experimental methods (XPS, ToF-SIMS, SFG, SPR, QCM-D, etc.) combined with computation methods (e.g., MD simulations) provide important information about the attachment, specificity, orientation, conformation and spatial distribution of surface immobilized proteins. This talk will discuss the significant progress has been made in developing surface analysis methods for characterizing the structure of surface immobilized proteins as well as the current challenges. Future protein characterization studies need to be extended to more complex samples as well as more tightly integrating complementary techniques that can be used to directly study immobilized proteins in the presence of the biological environment. In addition, further advances in computational methods for predicting protein-surface interactions and structures as well as providing structural information at the atomic level for large biomolecules is needed.

Manufacturing Science and Technology Group
Room: 5 & 6 - Session MS+AS-WeA

Advanced Surface, Interface, and Structural Characterization for High Volume Manufacturing

Moderator: Alain C. Diebold, Colleges of Nanoscale Science and Engineering, SUNY Polytechnic Institute

2:20pm **MS+AS-WeA1 The Cornell High Energy Synchrotron Source Upgrade: Current and Future Capabilities for Thin-film Research**, ***Arthur Woll***, Cornell University **INVITED**

In early 2019, the Cornell High Energy Synchrotron Source (CHESS) will complete its most significant upgrade since its construction in 1980. CHESS was originally constructed as a dual-purpose machine, serving as both an x-ray source as well as a particle physics experiment. Since 2008, CHESS has operated as one of only five dedicated high energy synchrotron sources in the world, and one of only two in the U.S.. The upgrade will result in a dramatically improved source, will include six new undulator-fed experimental stations, and represents a unique opportunity to increase and improve access to hard x-ray synchrotron light.

CHESS's history and mission emphasize the importance of deep collaboration with user communities to identify critical areas of instrumentation and methodological development. In particular CHESS has a long history of serving and advancing research on thin films and interfaces – in areas spanning both basic and applied research. CHESS currently hosts active user communities engaged in many of the most promising areas of thin-film research – including organic electronic thin films, high-K dielectrics and other complex oxides, dichalcogenides, and III-V nitrides. Particular research tools include ex-situ characterization such as grazing incidence small- and wide-angle scattering (GISAXS and GIWAXS), fast pole-figure analysis, automated x-ray reflectivity. Specialized equipment for in-situ measurements include chambers for in-situ thermal annealing and solvent annealing, and support for user-supplied UHV chambers for studying in situ thin-film growth and surface science. We will present several examples of recent user science as well as ongoing and proposed CHESS-based developments for thin-film research to motivate a discussion among the thin-film community of the most promising and critical areas for future capabilities of CHESS.

3:00pm **MS+AS-WeA3 Using Synchrotron XRD Techniques to Impact Microelectronics Manufacturing Technologies**, ***Jean Jordan-Sweet***, *C. Lavoie*, IBM T.J. Watson Research Center, *A.V. Carr*, IBM Research, Albany, NY, *N. Breil*, IBM SRDC, East Fishkill; now with Applied Materials Inc., *M.M. Frank*, IBM T.J. Watson Research Center **INVITED**

Since the early 1980s IBM has maintained a strong effort in synchrotron-based research. While our involvement with these facilities has been multi-faceted, we have leveraged our impact through two main avenues: the development of unique instrumentation and the nurturing of mutually beneficial collaborations with academia.

I will present examples of how synchrotron-based XRD studies have impacted our heavily materials- and process-centric technologies, preceded by a description of the instrumentation and techniques that were developed and applied in these examples. Much of our success in supporting IBM technology has been based on the use of *in-situ* XRD, electrical resistance, and optical light scattering measurements during the rapid thermal annealing of thin films or arrays of features. This instrumentation was developed at the NSLS (Brookhaven National Laboratory) [1], and has been redesigned, automated and recently installed at the Canadian Light Source. A second technique that is crucial for understanding the microstructure of thin polycrystalline films on single-crystal substrates is the measurement of texture. With the use of a linear or area detector, many high-resolution pole figures covering a large range of d-spacing can be obtained simultaneously [2]. Understanding and controlling film texture is critical to controlling phase transformations in thin films and to stabilizing and enhancing thermal processing windows during device manufacturing [3].

The first example is a long-term effort to understand the effects of materials and processing on the formation of low-resistance contacts to the gate, source and drain of CMOS devices. It has spanned three materials sets and many generations of chips. The culmination of this knowledge lies in a valuable database containing structure, roughness and resistance information from many thousands of anneals on key samples. With these measurements, IBM was able to extend the manufacturing lifetime of C54-TiSi$_2$, stabilize the NiSi process, and recently resolve a Ni "fang" defect [4] related to the IBM Power8® processor. The second example illustrates how the same techniques are helping us develop advanced memory devices based on ferroelectric hafnium oxide, which are intended to be used for neuromorphic computing.

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4:20pm **MS+AS-WeA7 Development of Ultra-thin ALD Grown high-k Dielectrics and Interconnect Diffusion Barrier Layers aided by Advanced X-ray Structural Analysis for sub 10nm Nodes**, ***Steven Consiglio***, *K. Tapily, R.D. Clark, C.S. Wajda, K.-H. Yu, T. Hakamata, G.J. Leusink*, TEL Technology Center, America, LLC, *S. Dey, A.C. Diebold*, Colleges of Nanoscale Science and Engineering, SUNY Polytechnic Institute **INVITED**

As the semiconductor industry develops processes and integration schemes for the 10nm technology node and beyond, conventional scaling of existing materials is no longer sufficient to enable further device scaling. New materials in the form of ultra-thin films need to be introduced and evaluated at an ever-increasing pace and conventional inline wafer metrology systems do not offer the needed flexibility and capabilities to probe the physical/chemical/structural properties of such extremely scaled layers of increasing complexity.

In this regard, we have investigated the properties of ultra-thin high-k dielectrics and interconnect (both Cu and Ru) diffusion barriers using advanced synchrotron X-ray structural analysis. Some key examples will be illustrated including analysis of higher-k phase stabilization and texturing in thin dielectrics on Si and high mobility substrates, ferroelectric phase stabilization for negative differential capacitance dielectrics, and the evaluation of diffusion barrier performance by using an in-situ ramp anneal method for both Cu and Ru which is a potential Cu interconnect replacement metal.

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S. Consiglio et al., *J. Electrochem. Soc*., **159**(6), G80-G88 (2012).

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5:00pm **MS+AS-WeA9 Stress Control of rf Sputter Deposition of Piezoelectric Sc$_{0.12}$Al$_{0.88}$N**, ***Michael Henry***, *R.P. Timon, T.R. Young, E.A. Douglas, B. Griffin*, Sandia National Laboratories

Substitution of Al by Sc has been predicted and demonstrated to improve the piezoelectric response with applications in radio frequency (RF) filter technologies. Although cosputtering has achieved Sc incorporation in excess of 20%, industrial processes require single target sputtering and is currently limited. However, the major concern with sputter deposition of ScAl is the control over growth of inclusions while simultaneously controlling film stress for suspended MEMS structures. Our work on 12% Sc suggests, with a direct relationship between the inclusion occurrences and compressive film stress, deposition control can suppress the inclusion growth by increasing the compressive stress. Too much compressive stress can prevent suspension of MEMS devices due to Euler buckling.

This work will describe the RF sputtering deposition and major parameter control over the deposition of Sc$_{0.12}$Al$_{0.88}$N. We will continue to show a multistep deposition which begins with a process of high compressive stress suppressing the inclusions and then drive the film back towards lower compressive stress levels such that an inclusion free low compressive stress film is deposited such that suspended resonators can be formed. To detail piezoelectric film properties, both top metal and top/bottom metal resonators are demonstrated from 500 MHz to 2 GHz.

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic

Room: 9 - Session SA+AS+HC+SS-WeA

In Situ and Operando Characterization of Interfacial Reactions in Energy & Electronic Devices

Moderators: Karen Chen-Wiegart, Stony Brook University/Brookhaven National Laboratory, Elke Arenholz, Lawrence Berkeley National Laboratory

2:20pm **SA+AS+HC+SS-WeA1 Probing Solid-Gas and Solid-Liquid Interface Using APXPS**, ***Zhi Liu***, *J. Cai, Q. Liu*, ShanghaiTech University, PR China, *Y. Han*, Chinese Academy of Sciences, PR China, *J. Liu*, ShanghaiTech University, PR China, *M. Mao, H. Zhang*, Chinese Academy of Sciences, PR China, *Y. Li*, ShanghaiTech University, PR China **INVITED**

Multiple new ambient pressure x-ray photoelectron spectroscopy (AP-XPS) endstations are currently under planning or development at US and international synchrotron light sources. Most of the research has been focused on the solid-gas interfaces. [1] Recently we have installed a new hard x-ray AP-XPS endstation at ALS Beamline 9.3.1 (2.5keV- 5keV). By using X-ray up to 5KeV, we can perform AP-XPS at a pressure up to 110 torr. The probing depth of photoelectrons also increases to >10 nm, which will allow us to study not only the gas/solid interface but also the liquid/solid interface. [2] In this talk, I will present results of in-situ studies on the electrolyte/electrode interface of a working model electrochemical cell. I will also give a brief introduction on the APXPS development in Shanghai.

We believe the successful development of soft and hard X-ray APXPS techniques will provide us and community beyond a powerful in-situ tool to directly study interface phenomena at Solid-Gas and Solid-Liquid Interfaces.

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3:00pm **SA+AS+HC+SS-WeA3 Graphene Capped Static and Fluidic Systems for In-Liquid Atmospheric Pressure XPS/AES/SEM and PEEM Studies of Electrochemical Interfaces**, ***Hongxuan Guo***, *E. Strelcov, A. Yulaev*, NIST, Center for Nanoscale Science and Technology, *S. Nemšák, D.N. Mueller, C.M. Schneider*, Peter Grünberg Institute and Institute for Advanced Simulation, Germany, *A. Kolmakov*, NIST, Center for Nanoscale Science and Technology

The liquid-solid electrochemical interfaces are a central topic of modern energy-related electrochemistry and catalysis research. For the last two decades, this research line benefited greatly from the development of differentially pumped electron optics and refreshable sample delivery systems which became an experimental core of the modern ambient pressure electron spectroscopy. An alternative experimental approach to atmospheric pressure electron microscopy (SEM[1], SPEM[2], PEEM[3]) and spectroscopy (XPS[4-5], XAS[3,6]) has been recently tested. In this approach, high electron transparency and molecular impermeability of the graphene membrane was employed to separate the liquid or gaseous sample from ultra-high vacuum environment of electron spectrometer.

In this presentation, we will show our recent work on design and performance of the static and fluidic microfabricated arrays (MCA) capped with bilayer graphene. With such a liquid cell, we characterized water and aqueous solution employing synchrotron-based and standard laboratory XPS, SEM, EDX, and Auger spectroscopy setups[7]. In particular, Cu electroplating and copper sulfate electrolyte polarization at the graphene working electrode have been studied spectroscopically in real time and nanoscopic spatial resolution.

Acknowledgement

ES, HG, and AY acknowledge support under the Cooperative Research Agreement between the University of Maryland and the National Institute of Standards and Technology Center for Nanoscale Science and Technology, Award 70NANB14H209, through the University of Maryland.

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3:20pm **SA+AS+HC+SS-WeA4 A 3D Printed Liquid Cell for Soft X-ray Absorption Spectroscopy**, ***Tom Regier***, *T.D. Boyko, J. Dynes, Z.N. Arthur*, Canadian Light Source, Inc., *M.N. Banis*, University of Western Ontario, Canada

Research methods that enable operando studies on energy materials are an important tool for the rational design of materials for renewable energy and carbon neutral technologies. Of particular value is the ability to observe the change in configuration of the 3d orbitals in transition metal based catalysts. Using the excitation of 2p electrons into vacant 3d orbitals, synchrotron based L-edge measurements allow for clear observation of chemical state and co-ordination geometry information from the first row transition elements. Challenges related to the operating in-situ flow cells in soft x-ray beamline endstations have been overcome and operando measurements are now possible at several facilities.

We report on the design of a 3D printed liquid flow cell with built-in electrodes for operando measurements of the transition metal L-edges. The disposable cells can be quickly customized for specific experiments and can be pre-ordered for lab-based characterization before attempting synchrotron measurements. Beamline instrumentation allows for highly sensitive fluorescence yield measurements with 10 micron spatial resolution or 1 minute time resolution.

4:20pm **SA+AS+HC+SS-WeA7 In Operando Quantification of Valence Changes in Memristive Devices**, *R. Dittmann*, ***Christoph Baeumer***, Peter Gruenberg Institute, Forschungszentrum Juelich GmbH, Juelich, Germany, *D. Cooper*, Université Grenoble Alpes & CEA, LETI, Minatec Campus, Grenoble, France, *C. Schmitz, S. Menzel, C.M. Schneider, R. Waser*, Peter Gruenberg Institute, Forschungszentrum Juelich GmbH, Juelich, Germany **INVITED**

Memristive devices based on resistive switching in transition metal oxides are attractive candidates for next-generation non-volatile memory applications. It is suspected that voltage-driven oxygen-ion migration and the resulting nanoscale redox processes drive the resistance change in these materials[1, 2]. Direct observation and quantification of the switching mechanism itself, however, remain challenging because the net changes of structure, stoichiometry, and valence state during switching are very small and occur primarily at electrode interfaces or within nanoscale filaments.

Here we will present local changes in the chemical and electronic structure of $SrTiO_3$-based memristive devices utilizing *in operando* characterization tools like transmission electron microscopy (TEM) and photoemission electron microscopy (PEEM). $SrTiO_3$ is chosen as a single crystalline model material, which offers a well-understood platform and well-characterized spectroscopic signatures.

To overcome the surface sensitivity typically limiting PEEM investigations of memristive devices, photoelectron-transparent graphene top electrodes are used to attain spectroscopic information from the buried $SrTiO_3$ layer[3]. During *in situ* switching, reversible changes of the O K-edge absorption spectra within spatially confined regions provide a quantitative map of the oxygen vacancy concentration, confirming that the resistance change is caused by localized oxygen evolution and reincorporation reactions rather than purely internal movement of oxygen vacancies[4].

A remarkable agreement between experimental quantification of the redox state and device simulation reveals that changes in oxygen vacancy concentration by a factor of 2 at electrode-oxide interfaces cause a modulation of the effective Schottky barrier and lead to >2 orders of magnitude change in device resistance. These findings allow realistic device simulations, opening a route to less empirical and more predictive design of future memory cells.

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5:00pm **SA+AS+HC+SS-WeA9 Magnetic Skyrmions in Ultrathin Magnetic Films and Nanostructures**, ***Jan Vogel***, Institut Néel, CNRS/UGA, Grenoble, France, *O. Boulle, R. Juge*, SPINTEC, CNRS/CEA/UGA, Grenoble, France, *D.S. Chaves, S. Pizzini*, Institut Néel, CNRS/UGA, Grenoble, France, *S.G. Je, G. Gaudin*, SPINTEC, CNRS/CEA/UGA, Grenoble, France, *T.O. Mentes, A. Locatelli*, Elettra-Sincrotrone Trieste, Italy, *M.U.J. Foerster, L. Aballe*, ALBA Synchrotron Light Facility, Spain **INVITED**

Magnetic skyrmions are chiral spin structures with a whirling spin configuration. Their topological properties, small size and sensitivity to small current pulses have opened a new paradigm for the manipulation of magnetization at the nanoscale. Chiral skyrmion were first experimentally observed in bulk materials [1] and in epitaxial ultrathin films [2], under a strong external magnetic field or at low temperature. More recently, it was predicted that they can also be created in thin magnetic films in stacks with structural inversion asymmetry [3]. We have used high lateral resolution PhotoEmission Electron Microscopy combined with X-ray Magnetic Circular Dichroism (XMCD-PEEM) to show that skyrmions with a size around 150 nm can indeed be stabilized at room temperature and without external magnetic field, in nanostructures of Pt/Co/MgO with a Co thickness of 1 nm [4]. The high sensitivity of the technique allows measuring very thin Co layers buried under protecting cover layers. The vectorial information obtained by rotating the sample with respect to the incoming x-ray direction allowed us obtaining information on the 3-dimensional spin structure of the skyrmions, directly showing the chiral spin configuration with left-handed chirality.

We investigated the dependence of the skyrmion size on an applied magnetic field, revealing that already a moderate field of 4 mT can reduce the skyrmion diameter to a size of 70 nm. We also studied the motion of skyrmions in micron-wide strips of Pt/Co/MgO induced by current pulses. The results show that skyrmions can be moved with moderate current pulses with current densities of some 10^{11} A/m^2, leading to velocities of several tens of m/s.

Our measurements show that synchrotron-based magnetic imaging using PEEM is very powerful for studying the static and dynamic properties of skyrmions in ultrathin magnetic films.

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5:40pm **SA+AS+HC+SS-WeA11 O_2 Pressure Dependence of SiO_2/Si Interfacial Oxidation Rate Studied by Real-time Photoelectron Spectroscopy**, ***Shuichi Ogawa***, Tohoku University, Japan, *A. Yoshigoe*, JAEA, Japan, *S. Ishidzuka*, National Institute for of Technology, Akita College, Japan, *Y. Takakuwa*, Tohoku University, Japan

Thermal oxidation of Si surfaces under the non-equilibrium conditions were used to form a high-quality Si oxide films and/or enlarge the oxidation rate. For example, rapid thermal oxidation (RTO) is performed under the raising the temperature, and then thick oxide can be formed without preventing the dopant diffusions[1]. In addition, the oxidation rate of RTO process is faster than that of constant temperature oxidation (CTO) though the highest temperature of RTO is as same as that of CTO[2]. Based on these knowledges, it is predicted that the oxidation rate at the SiO_2/Si interface can be quickened even by increase of the O_2 pressure. In this study, the increased O_2 pressure dependence of the interface oxidation rate which proceeds contentiously after Si(001) surface oxidation was investigated using real-tile photoelectron spectroscopy.

The oxidation experiment was performed using the surface reaction analysis apparatus placed at the BL23SU of SPring-8, Japan. A clean Boron doped p-type Si(001)2×1 surfaces were oxidized at 400°C under the O_2 pressure of 3.2×10^{-5} Pa. When clean surfaces were completely covered by the Si oxide, the O_2 pressure was elevated to P_{O2}(int) in order to enhance the interfacial oxidation. The P_{O2}(int) was changed between 6.4×10^{-5} Pa to 3.2×10^{-3} Pa. O 1s and Si 2p spectra were measured repeatedly during the oxidation. The time evolution of O 1s photoelectron intensity (I_{O1s}) was used for investigation of the oxidation rate.

From the I_{O1s}, we can estimate the completion of surface oxidation as 3200 s. An O_2 pressure was increased up to 1.5×10^{-3} Pa at this time, and then the interface oxidation was enhanced. The enhanced interfacial oxidation rates were obtained from the differential of I_{O1s}. The P_{O2}(int) dependence of the interfacial oxidation rate shows that the O_2 pressure increase makes the interfacial oxidation rate fast, and the interface oxidation rate is proportional to the square root of P_{O2}(int).

This result cannot be explained using traditional oxidation models, because the proportional relationship between the interface oxidation rate and square root of P_{O2}(int) indicates that the interface oxidation rate is limited by an O_2 diffusion through the oxide. However, the thickness oxide is much thinner than 1 nm, so that it cannot be thought that the rate-limiting reaction of interfacial oxidation is O_2 diffusion. To explain the kinetics, we propose the new interface oxidation model named "Unified Si oxidation model mediated by point defects"[3].

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6:00pm **SA+AS+HC+SS-WeA12 Highly Time-resolved Insights into the Sputter Deposition of Metal Electrodes on Polymer Thin Films for Organic Electronics**, ***Franziska Löhrer***, *V. Körstgens,* Technische Universität München, Germany*, M. Schwartzkopf,* Deutsches Elektronensynchrotron DESY, Germany*, A. Hinz, O. Polonskyi, T. Strunskus, F. Faupel,* Christian-Albrechts-Universität zu Kiel, Germany*, S.V. Roth,* Deutsches Elektronensynchrotron DESY, Germany*, P. Müller-Buschbaum,* Technische Universität München, Germany

With their easy processability, high flexibility and tuneable optical properties, organic electronics (OE) offer a wide range of potential applications. Especially photoactive polymers have received attention in recent years as candidates for organic photovoltaics (OPV) and light emitting diodes (OLEDs). Although based on organic materials, their electrodes are typically made from metals due to their unrivaled electronic conductivity. Thus, polymer-metal interfaces are inherently present in most OE devices and have a major influence on their behavior. Understanding the growth mechanisms of metal contacts on polymer thin films plays a crucial role in identifying potential ways to enhance the device performance. We investigate the morphological changes happening at the metal-polymer interface during the sputter deposition of metal contacts onto photoactive polymer films via in-situ grazing incidence small and wide angle x-ray scattering (GISAXS/GIWAXS) [1]. These techniques allow insights into the structural evolution of the metal on the organic film, which depends on various parameters such as the deposition rate or the film morphology. Making use of the brilliant synchrotron light source Petra III at DESY [2], we can study the deposition behavior of the metal on the polymer film with outstandingly high spatial and temporal resolution. The acquired large data sequences are tracked in real-time and further analyzed using the fast data reduction software DPDAK [3]. The final film morphology is characterized via scanning electron microscopy and X-ray reflectometry. UV/Vis absorption and reflection measurements complete our work. The metal layer formation can be described by applying an appropriate growth model based on our earlier work. [4] The model is refined in an iterative process of GISAXS simulations and data fitting. Comparing the deposition behavior of typical electrode materials on thin films of photoactive organic materials helps to understand their influence on the respective device performance.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Nanometer-scale crystals of the 2D oxide molybdenum trioxide (MoO_3) were formed atop the transition metal dichalcogenides MoS_2 and $MoSe_2$. The MoO_3 nanocrystals are partially commensurate with the dichalcogenide substrates, being aligned only along one of the substrate's crystallographic axes. These nanocrystals can be slid only along the aligned direction and maintain their alignment with the substrate during motion. Using an AFM probe to oscillate the nanocrystals, it was found that the lateral force required to move them increased linearly with nanocrystal area. The slope of this curve, the interfacial shear strength, was significantly lower than for macroscale systems. It also depended strongly on the duration and the velocity of sliding of the crystal, suggesting a thermal activation model for the system. Finally, it was found that lower commensuration between the nanocrystal and the substrate increased the interfacial shear, a trend opposite that predicted theoretically.

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

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

Applied Surface Science Division
Room: 13 - Session AS+BI+SA+SS-ThM

Spectroscopy of the Changing Surface
Moderators: Timothy Nunney, Thermo Fisher Scientific, UK, Tony Ohlhausen, Sandia National Laboratory

8:00am **AS+BI+SA+SS-ThM1 In Situ Investigation of the Dynamic Transformations of Model Catalyst Surfaces using Ambient Pressure XPS**, ***Iradwikanari Waluyo***, Brookhaven National Laboratory **INVITED**

In heterogeneous catalysis, the interaction between reactant molecules and the surface of the catalyst often causes changes in the surface composition and chemical state of the catalyst, which may result in changes in the reactivity of the catalyst. Using ambient pressure x-ray photoelectron spectroscopy (AP-XPS), these changes can be monitored in situ under close-to-realistic conditions. Unlike conventional XPS, which requires UHV conditions, AP-XPS measurements can be performed in the presence of gases at pressures of up to 100 Torr through the use differentially pumped analyzer, small analyzer entrance aperture, and x-ray transparent windows. Although AP-XPS measurements using lab x-ray sources are possible and becoming more common, experiments at modern synchrotron light sources have distinct and significant advantages including tunable photon energy, tightly focused beam, and better resolution. A general overview of the technique as well as recent experimental results will be presented. Examples shown include (1) the potassium-promoted reduction of $Cu_2O/Cu(111)$ by CO, in which the reduction of Cu^+ to Cu is accelerated by the presence of K through the formation of surface carbonate species, (2) the surface segregation of Pt/Cu(111) model bimetallic catalyst in the presence of various reactant gases, and (3) the reduction of $Cu_2O/Pt/Cu(111)$ by H_2.

8:40am **AS+BI+SA+SS-ThM3 Observation of Oxygen Binding on PGM-free Electrocatalysts by Ambient Pressure XPS and XAS**, ***Kateryna Artyushkova***, University of New Mexico, *M.J. Dzara, S. Pylypenko*, Colorado School of Mines, *P. Atanassov*, University of New Mexico

The most promising class of PGM-free materials for oxygen reduction reaction (ORR) is based on graphene-like carbon containing nitrogen and transition metal (MNC). They show promise as replacement of Pt in two different technological platforms - alkaline exchange membrane fuel cells (AEMFCs) and proton exchange membrane fuel cells (PEMFC). It is well established that nitrogen coordination with metal in the carbon network of MNC materials is directly related to ORR activity; however, the ***exact nature of the active sites*** is still debated even after over 50 years of research. Understanding the specific roles of nitrogen and metal in the properties/activity/stability/durability of MNC-based catalytic materials is a prerequisite for the rational design of ORR electrocatalysts with improved performance.

The key component in elucidating the relationship between the chemistry of active sites and activity is a better understanding of the formation of adsorbates, intermediates, and products during reactions occurring within the fuel cell.

In situ monitoring reaction steps under realistic conditions in metal-free and metal-containing building blocks will shed light onto the reaction mechanism that is essential for developing active and durable PGM-free catalyst for ORR.

We will report on AP-XPS analysis for series of electrocatalysts belonging to Fe-N-carbon families based on sacrificial support method (SSM) and Metal-organic frameworks (MOF). The effect the nitrogen chemistry and the type of iron have on the oxygen binding was investigated by ambient pressure X-ray Photoelectron Spectroscopy (XPS) and X-ray Adsorption Spectroscopy (XAS) under an O_2 environment at operating temperature of the fuel cell. The effect of the relative abundance of different types of nitrogens, such as pyridinic, coordinated to iron and hydrogenated nitrogens (pyrrolic and hydrogenated pyridine) on the preference of oxygen binding is studied by high-resolution nitrogen photoelectron spectra. The role of metallic and atomically dispersed iron will be investigated by a combination of XAS and XPS. Linking differences in oxygen binding to the differences in the chemistry of the electrocatalysts are of ultimate importance for elucidating the oxygen reduction reaction mechanism.

1. Artyushkova, K., et al., *Oxygen Binding to Active Sites of Fe–N–C ORR Electrocatalysts Observed by Ambient-Pressure XPS.* The Journal of Physical Chemistry C, 2017. **121**(5): p. 2836-2843.

9:00am **AS+BI+SA+SS-ThM4 In situ Monitoring of Electrochemically Generated Carbene by XPS**, ***Pinar Aydogan Gokturk****, *S.E. Donmez, Y.E. Turkmen, B. Ulgut, S. Suzer*, Bilkent University, Turkey

Ionic liquids provide a platform for fundamental electrochemical studies in vacuum. In this present work, we report an in-situ X-ray photoelectron spectroscopic (XPS) investigation of N-heterocyclic carbene(NHC) generation from the electrochemical reduction of imidazolium based ionic liquids (ILs) through changes in oxidation state of nitrogen atoms. The IL serves as an electroactive material as well as the electrolyte in the cell between a Si substrate which is connected to the instrument ground and a gold wire connected to the sample holder for electrical connection. Through the course of the electrochemical reaction, the positive charge on imidazolium cation is neutralized to give free NHC as reflected by the distinct shifts in the N 1s and C 1s binding energies. The observations are further supported by colorful adduct formation of carbenes with CS_2, reversible redox peaks in the voltammogram and the density functional theory calculations. The presented structure and XPS measurements can lead on understanding of the mechanism for various electrochemical reactions.

9:20am **AS+BI+SA+SS-ThM5 The Influence of Water on the Ionic Liquid-Vapor Interface**, ***John Newberg***, University of Delaware, *M.B. Shiflett*, University of Kansas, *A. Broderick, Y. Khalifa*, University of Delaware

Ionic liquids (ILs) have a wide array of applications in biotechnology, coatings, synthesis, separations, and energy sciences. Many of these processes involve either IL-solid or IL-vapor interactions and it is important we understand the fundamental interfacial properties of ILs on a molecular level. Due to the ubiquity of water and the hydrophilic nature of ILs, water can either be unintentionally present or often intentionally added to alter IL properties including density, viscosity, friction and electrochemical window. In this talk we will highlight our recent efforts examining the IL-water vapor interface utilizing ambient pressure X-ray photoelectron spectroscopy (APXPS). APXPS allows for a molecular level assessment of the IL-vapor interface including a quantitative assessment of interfacial water concentration, moiety specific electronic environment changes, structural changes and obtaining adsorbate energetics.

9:40am **AS+BI+SA+SS-ThM6 Ambient Pressure XPS Studies of Model N-C and Fe-N-C Catalysts Under Oxygen Environment**, ***Michael Dzara***, Colorado School of Mines, *K. Artyushkova*, University of New Mexico, *C. Ngo, M.B. Strand, J. Hagen, S. Pylypenko*, Colorado School of Mines

Producing inexpensive polymer electrolyte membrane fuel cells requires significant reduction in the amount of platinum group metal (PGM) oxygen reduction reaction (ORR) catalyst used. High surface area iron- and nitrogen-functionalized carbon (Fe-N-C) materials are a promising PGM-free replacement. These catalysts are very heterogeneous, leading to difficulties in discerning contributions from various potential active sites and identifying the most active species.[1] Techniques such as scanning transmission electron microscopy (STEM), energy dispersive x-ray spectroscopy (EDS), and x-ray photoelectron spectroscopy (XPS) provide structural and chemical information that can be correlated to ORR activity measured with electrochemical methods. Ambient pressure XPS (AP-XPS) and x-ray absorption spectroscopy (XAS) conducted in a humidified O_2 environment, at an elevated temperature, and with applied potential offer opportunities to study materials under *in situ* conditions to determine adsorbates, intermediates, and products during ORR steps.[2,3]

In this work, model Fe-N-C catalysts are studied along with reference nitrogen-doped carbon (N-C) materials. Development of model catalyst materials with controlled morphology and speciation can simplify the elucidation of active sites. Micro-porous N-C nanospheres with high graphitic content were synthesized by a solvothermal treatment of resorcinol, formaldehyde, and ethylenediamine, and a subsequent pyrolysis in N_2.[4] Incorporation of Fe into the N-C nanospheres was carried out by wet-impregnation of various Fe precursors followed by a second N_2 pyrolysis. By varying synthetic parameters, a set of N-C and Fe-N-C nanospheres with diverse compositions and properties were produced. Differences in composition and structure were evaluated using STEM-EDS and XPS, demonstrating control over N and Fe quantity and speciation. Select N-C and Fe-N-C nanospheres were then characterized with *in situ* AP-XPS, and in the case of Fe-N-C nanospheres, *in situ* XAS. By understanding the ORR on

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* **ASSD Student Award Finalist**

these model Fe-N-C nanospheres, synthesis-property-performance conclusions are drawn, guiding the development of highly active Fe-N-C catalysts.

[1] A. Serov, K. Artyushkova, E. Niangar, C. Wang, N. Dale, F. Jaouen, M.-T. Sougrati, Q. Jia, S. Mukerjee, and P. Atanassov, Nano Energy **16**, 293 (2015).

[2] K. Artyushkova, I. Matanovic, B. Halevi, and P. Atanassov, J. Phys. Chem. C **121**, 2836 (2017).

[3] Q. Jia, N. Ramaswamy, H. Hafiz, U. Tylus, K. Strickland, G. Wu, B. Barbiellini, A. Bansil, E.F. Holby, P. Zelenay, and S. Mukerjee, ACS Nano **9**, 12496 (2015).

[4] N.P. Wickramaratne, J. Xu, M. Wang, L. Zhu, L. Dai, and M. Jaroniec, Chem. Mater. **26**, 2820 (2014).

11:00am **AS+BI+SA+SS-ThM10 Real-time Photoelectron Spectroscopy Observation of Oxidation and Reduction Kinetics of Ni(111) Surface**, ***Ryo Taga***, *S. Ogawa*, *Y. Takakuwa*, Tohoku University, Japan

Nitrogen contained in the air is oxidized and then harmful nitrogen oxide (NO_X) is formed in the combustion chamber of engine. Accordingly, the exhaust gas which contains NO_X is purified by catalysts. However, platinum group metals, whose prices are likely to rise by the depletion of resources in the future, are used as the catalysts, so the reduction of the amount used is an important matter for industrial and environmental fields. On the other hand, it has been already known that Ni has an effect to NO_X reduction, but the its catalytic ability disappears when the Ni surface is oxidized. If O atoms on the Ni surface can be efficiently desorbed, Ni is expected as a catalyst for NO reduction. In the previous studies, some of researches have studied about reduction of oxidized Ni surfaces, but the relation between oxide reduction kinetics and behavior of O atoms has not yet been clarified. In this study, the oxidation and reduction kinetics on Ni(111) surfaces was investigated by real-time ultraviolet photoelectron spectroscopy (UPS). to investigate the amount of O atom adsorption and the changes of work function.

The experiments were performed using UPS apparatus with base pressure of ~3×10^{-8} Pa. The Ni(111) surface was firstly cleaned by the Ar^+ ion bombardment, and the annealed at 600℃. O_2 gas (1×10^{-5} Pa) was directly introduced to UPS apparatus at the sample temperature of 100℃. After the end of the introduction of O_2 gas, the sample heated up to and H_2 gas (1×10^{-5} Pa) was introduced in order to investigate the Ni oxide reduction process. The photoelectron spectra were measured repeatedly each 72 s during oxidation and reduction.

From the time evolution of O 2p photoelectron spectra, we obtained the O 2p uptake curve and the change in work function. When O_2 gas was introduced, O 2p intensity increases linearly, so it turned out that the oxidation of Ni(111) surfaces was a zero order reaction. After introduction of H_2 gas, O 2p intensity decreases gently for about 500 s and then decreased rapidly. On the other hand, the work function slightly increased and then rapidly decreased. The work function reaches the same value on the clean Ni(111) surface. Therefore, Ni oxide can be reduced completely using H_2 gas.

These changes after introduction of H_2 gas can be divided into two areas. In the first area, O atoms are drawing from subsurface because of slight increase of work function. In the second area, then, it is suggested that the reduction progresses and the clean Ni surface area enlarges as like to island growth. In the symposium, we will discuss the reduction process of the oxidized Ni surface by NO gas.

11:20am **AS+BI+SA+SS-ThM11 Comparison of Initial Oxidation Kinetics between p- and n-type Si(001) Surfaces Studied by Real-time Photoelectron Spectroscopy**, ***Yuki Sekihata***, *S. Ogawa*, Tohoku University, Japan, *A. Yoshigoe*, JAEA, Japan, *R. Taga*, Tohoku University, Japan, *S. Ishidzuka*, National Institute of Technology, Akita College, Japan, *Y. Takakuwa*, Tohoku University, Japan

An oxidation reaction is the "trade" of electrons between oxygen and other materials, therefore it is thought that there is a difference in the oxidation kinetics on between p-type and n-type Si substrates. In the previous researches about the kinetics of the thermal oxidation of Si, the oxidation rate have not taken account of the difference of conduction type because the thermal oxidation was performed in high temperature region above 600℃ named intrinsic region where the intrinsic carrier concentration becomes comparable to the donor or acceptor concentration. On the other hand, oxidation temperature becomes lower to form thin oxide films below 1nm. Therefore, we believe that the difference of conductivity affects an oxidation kinetics on the Si(001) surfaces, but there is no oxidation reaction models that takes into account the difference of conductivity. In this study, we investigated the oxidation reaction kinetics on p- and n-type Si surfaces using real-time ultraviolet photoelectron spectroscopy.

The samples for oxidation were p-Si(001) and n-Si(001) surfaces. The dopants were Boron and arsenic for p- and n-type substrates, respectively. Their density of dopants were approximately 10^{18} atoms/cm^3 so extrinsic region can be kept in the high temperature region even below 700℃. These samples were oxidized using O_2 gas at the pressure of 1.0×10^{-5} Pa. During the oxidation reaction, the photoelectron spectra were measured repeatedly, therefore time evolution of the amount of oxygen adsorption, work function, and band bending can be investigated.

In the room temperature oxidation, it is found that oxidation reaction coefficient on n-Si(001) is larger than that on p-Si(001). To clarify the reasons, we focus to the changes of work function due to the formation of dipole layer. The work function of the n-Si(001) surface shows negative value but p-Si(001) is positive value. From this result, we can estimate the adsorption positions of O atoms. O atoms have a negative charge in the bond of Si-O, so it can be assumed that oxygen is placed on the n-Si(001) surfaces, but it is subsurface in case of the p-Si(001) surface. In case of n-Si(001) substrates, the doped electrons spill out into the surface because many electrons exist in the substrate. As the result, oxidation reaction is promoted in the n-Si(001) surface. From these results, we found that there is a difference of oxidation kinetics depending on the conductivity. In the presentation, we will show also the difference of oxide states between them.

11:40am **AS+BI+SA+SS-ThM12 Co-Pyrphyrin on Cu_2O(111) and TiO_2(110): Properties and Stability under Near Operando Conditions**, ***Zbynek Novotny***, *W.-D. Zabka*, *M. Hotz*, *D. Leuenberger*, University of Zurich, Switzerland, *L. Artiglia*, *F. Orlando*, *M. Ammann*, Paul Scherrer Institut (PSI), Switzerland, *J. Osterwalder*, University of Zürich, Switzerland

The pyridine-based macrocycle Co-pyrphyrin (Co-Pyr) is a promising molecular water reduction catalyst recently synthesized at the University of Zurich [1]. We investigated Cu_2O(111) and TiO_2(110) substrates covered with a complete monolayer of Co-Pyr at pressures spanning from ultra-high vacuum (UHV) up to near ambient pressures of 1 mbar of water vapor. To study the surface photovoltage (SPV) effect, samples were illuminated with UV laser light through the electron spectrometer lens system. Both under UHV and water pressures up to 1 mbar, SPV-induced shifts of the order of ΔE_k = +120 meV were observed in case of Cu_2O(111), while for TiO_2(110), much smaller SPV shifts of -0.12 meV were observed. X-ray absorption spectroscopy (XAS) of the Co L3-edge in dependence of illumination and water exposure was used to monitor the electronic structure of the Co metal center of Co-Pyr molecules. Comparison to simulated XAS spectra reveals that on the TiO_2(110), the Co centers partially transform from a +2 to +1 oxidation state upon exposure to water, while on the Cu_2O(111), the Co remains in the +2 oxidation state irrespective of the water exposure. Our measurements provide insights into the stability and behavior of the Co-Pyr molecules studied under near operando conditions, further stimulating the use of these molecular catalysts in the next-generation of solar fuel cells.

[1] Joliat, E et al., *Dalton Transactions* **2016,***45* (4), 1737-1745.

Biomaterial Interfaces Division
Room: 12 - Session BI+AS+SA-ThM

Characterisation of Biological and Biomaterial Surfaces
Moderators: Daniel Graham, University of Washington, Tobias Weidner, Aarhus University, Denmark

8:00am **BI+AS+SA-ThM1 Lipid Involvement in the Regenerative Processes of *Dugesia dorotocephala* - A GCIB ToF-SIMS Imaging Study**, ***Tina Angerrer***, *M.J. Taylor*, *D.J. Graham*, *L.J. Gamble*, University of Washington

Dugesia dorotocephala are planaria belonging to the class of Turbellaria, or non-parasitic flat worms. They are best known for their fascinating regenerative abilities, which allow them to be cut into more than 200 pieces, each piece missing essential parts necessary for the worms' survival and each re-growing a new flatworm. This level of reorganization involves a complex interplay of a wide range of molecules that varies spatially and temporally but is still poorly understood.

Recently the involvement of peptides and proteins in the process of regrowing the head and developing a new central nervous system has been studied by Sweedler et al.[1] using MALDI imaging. MALDI, in contrast to TOF-SIMS imaging, is capable of studying the distributions of peptides in tissue but spatial resolution is limited and molecules of interest have to be partially predetermined by the choice of matrix.

Using the J105-3D Chemical Imager, (Ionoptika Ltd) equipped with a 40 keV gas cluster ion beam (GCIB), molecules with sizes up to 2000 Da can be localized at a cellular scale, with spatial resolutions better than 3 µm.[2] Since ToF-SIMS is a label free technique, it can be used in an untargeted discovery approach which, in biological samples, is mainly used to study lipid distributions.

Lipids are a diverse group of molecules fulfilling numerous functions such as energy storage and cell signaling, however lipid and fatty acid data for Dugesia in general is very limited and their localizations completely unknown.[3] Our studies were targeted at establishing a full body lipid profile for the different organ systems present in Dugesia as well as monitoring their changes due to stem cell migration during head regrowth and eye/CNS regeneration.

Dugesia flatworms were sectioned on a cryomicrotome at -20 °C and slices were placed on ITO coated glass. After preparation samples were immediately taken to the lab for analysis. Sample preparation and transport time was kept to less than 2 hours to minimize lipid degradation. After SIMS analysis, optical images were acquired in order to facilitate identification of structures seen within the worms. To deal with the increased spectral and spatial complexity provided by our improved instrumental capabilities, imaging PCA was used to “untangle” the data. In this presentation we will present the results of our studies showing the unique lipid distributions throughout Dugesia cross sections and discuss their relevance.

[1] T. H. Ong, *et al.*, J Biol Chem 2016, 291, 8109-8120.

[2] T. B. Angerer, *et al.*, Int J Mass Spectrom 2015, 377, 591-598.

[3] F. Meyer, *et al.*, Biochim Biophys Acta 1970, 210, 257-&.

8:20am **BI+AS+SA-ThM2 Can ToF-SIMS Imaging Explain Biology?**, ***Lara Gamble***, *D.J. Graham*, University of Washington

Imaging time-of-flight mass spectrometry (ToF-SIMS) can provide images of cells and tissues with chemical and molecular specificity. These chemically specific images could revolutionize our understanding of biological processes such as the role of changes in tumor metabolism affecting the response to chemotherapy is under scrutiny. Regions of interest (ROIs) of the tumor can be utilized to compare similar regions from different tissue samples. PCA analysis of ToF-SIMS image data reveals the differences in chemistries between the regions. These results help to identify links between the chemical composition within and around tumors and the changes of these tumors as a response to the treatment. However, often the presentation of ToF-SIMS results might not be in the best format to gain the interest of non-SIMS scientists. Different data processing and data presentation format from clinical trial tissue samples and other tissue samples analyzed with ToF-SIMS will be presented. Additional validation of data interpretation from different techniques will be discussed.

8:40am **BI+AS+SA-ThM3 Applications of XPS for Novel Biomaterial Systems**, ***Jonathan Counsell***, *S.J. Coultas, C.J. Blomfield*, Kratos Analytical Limited, UK, *C. Moffitt*, Kratos Analytical, *S.J. Hutton*, Kratos Analytical Limited, UK **INVITED**

XPS is widely used in the field of biomaterials yielding quantitative elemental and chemical state information [1]. It is possible to identify changes in functional groups present both on the surface and, combined with depth profiling, within the bulk of a biomaterial.

Here we will discuss the latest advancements in XPS as applied to a range of biomaterial systems and examine new possibilities beyond routine spectroscopic analysis. Non-destructive depth profiling of the near surface region is applied to ultra-thin films examining growth modes and film closure mechanisms. With the dual Al/Ag monochromated sources it is possible to vary information depth for relative comparisons on the nature of the uppermost layers. New developments in cluster ion sources now allow soft biomaterials to be depth profiled. Accurate analysis of interfacial chemistry is possible without ion beam damage. XP Imaging will also be discussed for systems exhibiting surface inhomogeneity. Quantitative images yield useful additional information over conventional microscopies. Discussions will concentrate on both model systems and real life applications highlighting the latest possibilities of XPS for this growing field.

[1] Donald R. Miller and Nikolaos A. Peppas, Journal of Macromolecular Science, Part C Vol. 26 , Iss. 1,1986

9:20am **BI+AS+SA-ThM5 Surface Characterization of Polymer Scaffolds: Understanding Surface Modification and Biological Interactions**, ***Michael Taylor***, University of Washington, *M.J. Hawker, M.N. Mann*, Colorado State University, *G.E. Hammer*, University of Washington, *E.R. Fisher*, Colorado State University, *D.J. Graham, L.J. Gamble*, University of Washington

Biopolymers show increasing usage in medical device technologies including joint replacement, stents and tissue engineered supports. (polymer scaffolds). Barriers to successful use of biopolymer usage for medical devices can include ineffective interaction of biological systems with the biopolymer and biofilm formation. Historically, developing medical devices with antibacterial properties have involved inclusion of silver or copper dopants as they facilitate bacterial membrane rupture. Bacterio-static coatings provide an alternative approach by generating a hydrophobic surface that prevents colonisation by reversible adhesion via van der Waals forces prior to anchoring strongly with adhesion structures such as pili. Plasma enhanced chemical vapor deposition (PECVD) is a cheap yet powerful method of introducing chemical functionalities to surfaces as the low temperature high energy process may be used to couple a variety of monomers to biomaterial surfaces. Previous evidence provided by Fisher and coworkers showed that PECVD may be utilised to produce antifouling coatings by modifying polycaprolactone (PCL) with fluorinated organic compounds[1], however the porous morphology of scaffolds required for vascularisation also provides multiple points of attachment for the critical first step in biofilm formation. It is therefore necessary determine the effectiveness of PECVD throughout the scaffold. For this we employ time-of-flight secondary ion mass spectrometry (ToF-SIMS) and X-ray photoelectron spectroscopy (XPS) to analyse the surface modification of porous polymer scaffolds.

ToF-SIMS imaging coupled with X-ray photoelectron spectroscopy (XPS) provides a powerful combination of high resolution imaging and elemental quantitative analysis that allows a detailed analysis of the surface. Herein we apply this combination of analysis methods for the determination and quantification of fluorocarbon distribution across a PCL scaffold modified with octafluoropropane by PECVD, determining that a treatment time of 20 minutes Introduces a homogeneous distribution of fluorocarbon film throughout the construct cross section whereas lower treatment times produces a gradient distribution of fluorocarbon, as measured via CF^+ and CF_3^+ signals

(1) Hawker, M. J.; Pegalajar-jurado, A.; Fisher, E. R. Conformal Encapsulation of Three-Dimensional, Bioresorbable Polymeric Sca Ff Olds Using Plasma-Enhanced Chemical Vapor Deposition. **2014**.

9:40am **BI+AS+SA-ThM6 Seawater Bacteria on Technical Surfaces: Lateral and Vertical Adhesion Forces and Nanomechanical Properties**, *N. Davoudi, K. Huttenlochner*, University of Kaiserslautern, Department of Physics and Research Center Optimas, Germany, *C. Schlegel, M. Huster*, University of Kaiserslautern, Institute of Bioprocess Engineering, Germany, ***Christine Müller-Renno***, University of Kaiserslautern, Department of Physics and Research Center Optimas, Germany, *R. Ulber*, University of Kaiserslautern, Institute of Bioprocess Engineering, Germany, *C. Ziegler*, University of Kaiserslautern, Department of Physics and Research Center Optimas, Germany, Germany

Biofilms are often unwanted, but can also be utilized in biofilm reactors. In such a reactor different forces act on the cells: lateral forces by flow, forces perpendicular to the interface which dominate the first contact and the biofilm formation, and forces on the cell-wall by turgor pressure which influence the viability of the cells. The interplay of these forces plays a major role in the establishment of a biofilm.

Here, we report on the seawater bacterium *Paracoccus seriniphilus* on titanium and glass. Microstructured titanium is our substrate of choice in the reactor. We hence have to understand the influence of wettability, roughness, defined structures, and environmental conditions such as pH and ionic strength on the viability as well as the bacterial attachment and detachment.

In a first set of experiments, the turgor pressure of the bacteria was determined as a function of pH and salinity by measuring force-distance curves with a scanning force microscope (SFM). As a seawater bacterium, *P. seriniphilus* can easily adapt to saline conditions and can survive at NaCl concentrations up to 100 gL^{-1}. Depending on the ionic strength the turgor pressure and thus the elasticity and size of the cell changes. *P. seriniphilus* has its optimum pH at 7, but at pH 4 the results point to an active adaption mechanism to acidic conditions. The results at pH 11 show that *P. seriniphilus* cannot adapt to alkaline conditions.

As next step the vertical adhesion forces of a single bacterium were measured as a function of pH, ionic strength, and substrate. The adhesion force of one single cell decreases from pH 4 to pH 9. As a function of the ionic strength, the adhesion forces increase with increasing salt concentration with a pronounced spike (higher adhesion forces) at 0.9 % NaCl. All adhesion force changes completely correlate with the electrostatics as determined by zetapotential measurements. A conditioning film of growth medium strongly decreases the attachment forces. Thus the first bacterial layer should grow without medium at pH 4.

In a last step, the lateral detachment forces of the bacteria were measured. There is a clear correlation between the applied force and the number of moved bacteria, but the detachment forces vary for the individual bacteria. For small lateral forces (0.5 nN), the wettability of the substrate seems to control the detachment process. For higher lateral forces (2-3 nN), the effect of the wettability gets lost and the roughness of the samples controls the cell detachment. These detachment forces are in the same range or higher than the shear forces applied by the fluid flow.

11:00am **BI+AS+SA-ThM10 AVS 2017 Peter Mark Memorial Award Lecture: A Combined Experimental–Simulation Approach for Unraveling Hydrophobic Interactions at the Molecular Scale**, *P. Stock,* MPI for Iron Research, Germany, *J.I. Monroe,* UC Santa Barbara, *T. Utzig,* MPI for Iron Research, Germany, *D.J. Smith, M.S. Shell,* UC Santa Barbara, ***Markus Valtiner****, TU Bergakademie Freiberg, Germany **INVITED**

Interactions between hydrophobic moieties steer ubiquitous processes in aqueous media, including the self-organization of biologic matter. Recent decades have seen tremendous progress in understanding these for macroscopic hydrophobic interfaces. Yet, it is still a challenge to experimentally measure hydrophobic interactions (HIs) at the single-molecule scale and thus to compare with theory.

Here, I will present a combined experimental–simulation approach to directly measure and quantify the sequence dependence and additivity of HIs in peptide systems at the single-molecule scale. We combined dynamic single-molecule force spectroscopy on model peptides with fully atomistic, both equilibrium and nonequilibrium, molecular dynamics (MD) simulations of the same systems. Specifically, we mutate a flexible (GS)$_5$ peptide scaffold with increasing numbers of hydrophobic leucine monomers and measure the peptides' desorption from hydrophobic self-assembled monolayer surfaces. Based on the analysis of nonequilibrium work-trajectories, we measure an interaction free energy that scales linearly with 3.0–3.4 k_BT per leucine. In good agreement, simulations indicate a similar trend with 2.1 k_BT per leucine, while also providing a detailed molecular view into HIs.

Our approach potentially provides a roadmap for directly extracting qualitative and quantitative single-molecule interactions at solid/liquid interfaces in a wide range of fields, including interactions at biointerfaces and adhesive interactions in industrial applications. In this context, I will finally discuss in detail how single molecule unbinding energy landscapes can be utilized to predict scenarios where a large number of molecules simultaneously interact, giving rise to adhesive failure under corrosive and wet conditions.

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11:40am **BI+AS+SA-ThM12 Quantitative Characterization of Bacterial Cells in Solution and on Surfaces**, *C. Sousa, K. Jankowska, L. Parga Basanta, I.M. Pinto,* ***Dmitri Petrovykh***, International Iberian Nanotechnology Laboratory, Portugal

Physicochemical properties of bacterial cells make them challenging subjects for methods typically used to characterize micro- and nanoparticles. Even for conceptually simple parameters, such as size and concentration, direct characterization of live bacteria (and their agglomerates) in solution is far from trivial because bacterial cells are soft and often anisotropic particles with sizes of not more than a few microns. Low contrast, in terms of optical and electronic properties, between bacteria and their aqueous environment complicates any attempted direct measurements in solution. Comparing bacterial cells to non-biological micro- or nanoparticles, whether in the context of mixed samples or calibration measurements, further compounds the complexity of characterizing these systems.

We are using *Staphylococcus aureus* (*S. aureus*) bacteria as a model system for quantitative characterization of bacterial cells. For systematic measurements, *S. aureus* bacteria offer the advantages of nearly spherical shape and of robust viability under a wide range of experimental conditions and treatments. The approximately one micron diameter of live *S. aureus* cells also makes them representative of the sensitivity and resolution challenges encountered in the characterization of bacterial cells. In microscopy, for example, the apparent size of individual *S. aureus* bacteria changes dramatically as they are prepared for measurements with increased spatial resolution: from confocal optical microscopy, to environmental scanning electron microscopy (SEM), to SEM in vacuum.

The objective of our work is to develop and validate a set of complementary techniques that can be used to characterize live bacterial cells. We will describe the use of nanoporous membranes with *S. aureus* suspensions and commonly overlooked effects of centrifugation, mechanical agitation, and other typical sample preparation procedures on the apparent distribution and properties of particles in biological samples. The forced contact of bacteria with these membranes during filtering also suggests their use as model systems for investigating the interactions of bacteria with surfaces having different chemistries and/or morphological features.

12:00pm **BI+AS+SA-ThM13 *In Situ* Multimodal Imaging of Microbial Communities**, ***Xiao-Ying Yu***, Pacific Northwest National Laboratory

We developed a vacuum compatible microfluidic interface, System for Analysis at the Liquid Vacuum Interface (SALVI), to enable direct observations of liquid surfaces and liquid-solid interactions using time-of-flight secondary ion mass spectrometry (ToF-SIMS) and a variety of spectroscopy and microscopy characterization techniques. SALVI was recently applied to investigate biological interfaces in living biofilms and co-cultured microbial communities. In this talk, two case studies will be presented using in situ liquid ToF-SIMS, light microscopy, and fluorescence microscopy. In the first case study, *Shewanella* wild type and mutant were both exposed to environmental stressors such as toxic heavy metal ions (i.e., Cr (VI)) and silver nanoparticles. The response of biofilm and its extracellular polymeric substance (EPS) to the environmental perturbation was investigated using in situ liquid SIMS coupled with structured illumination microscopy (SIM). In the second case, a more complex microbial communities consisting of syntrophic *Geobacter metallireducens* and *Geobacter sulfurreducens* was investigated. Electron donor and electron acceptor in this co-cultured microbial system were characterized first using the more traditional SIMS dry biological sample preparation approach followed by in situ liquid SIMS and confocal laser scanning microscopy (CLSM). The electron transfer between the two species was probed dynamically using the electrochemical SALVI. Correlative imaging is employed to achieve a more holistic view of complexed microbial systems across different space scales. Our results demonstrate that interfacial chemistry involving living microbial systems can be studied from the bottom up based on microfluidics, potentially providing more important understanding in system biology.

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

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

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

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

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

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

One of the most interesting characteristics of alloy nanoparticles (NPs) is that they can have different phases from those of the bulk. In the bulk phase diagram of Pd$_x$Cu$_{1-x}$, there exists a composition range, $0.35 < x < 0.55$, over which a B2 phase (ordered body centered cubic, CsCl structure) is formed at T < 873 K, in spite of the fact that pure Pd and Cu both have face centered cubic (FCC) bulk crystal structures. An experimental methodology has been developed for determining the phase behavior of Pd$_x$Cu$_{1-x}$ size and composition spread nanoparticle (SCSNP) libraries. Spatially resolved X-ray photoemission spectroscopy (XPS) was used to map the Cu $2p_{3/2}$ core level

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* **Peter Mark Memorial Award Winner**

shifts (CLS) with respect to the value for pure Cu across composition space on the bulk $\mathrm{Pd}_x\mathrm{Cu}_{1-x}$ alloy. The result has shown that the Cu 2$p_{3/2}$ binding energy decreases monotonically with increasing Pd at.% in the FCC phase. There is additional discontinuous CLS over the composition range from 0.35 to 0.55 Pd at.%, where the B2 phase forms. Therefore, the Cu 2$p_{3/2}$ core level binding energy measured by XPS can be used to distinguish between the ordered B2 phase and disordered FCC phase. The $\mathrm{Pd}_x\mathrm{Cu}_{1-x}$ SCSNP library on a Mo substrate was prepared using a rotatable shadow mask deposition tool previously developed by our group. After annealing the $\mathrm{Pd}_x\mathrm{Cu}_{1-x}$ alloy thin film to 700 K, the additional CLS over the composition range, $0.35 < x < 0.55$, has been observed at a film thickness > 6 nm, which suggests the formation of B2 phase. However, at a film thickness between 4 – 6 nm, the Cu 2$p_{3/2}$ binding energy decreases monotonically across composition space which suggests that only FCC phase exists for alloy films in this thickness range. Because the FCC phase is more densely packed than the B2 phase, the surface tension in this thickness regime can drive a conversion from the ordered B2 phase back to the randomly distributed FCC solid solution. More interestingly, the additional CLS over the composition range from 0.35 to 0.55 Pd at.% reoccurs at a film thickness < 4 nm, which suggests the formation of B2 phase. This observation is the result of dewetting of the $\mathrm{Pd}_x\mathrm{Cu}_{1-x}$ NPs after heating at 700 K for 30 mins, and the size of dewetting NPs exceeds 6 nm where the close-packed FCC phase is stabilized. Dewetting of $\mathrm{Pd}_x\mathrm{Cu}_{1-x}$ NPs is validated by the appearance of the substrate Mo XPS signal at a film thickness < 4 nm. This comprehensive experimental study of the phase behavior for $\mathrm{Pd}_x\mathrm{Cu}_{1-x}$ alloy NPs will be correlated with their catalytic activity across composition and size spaces to accelerate the development of alloy NPs for catalytic applications.

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

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

We have designed and built a unique platform that allows us to concurrently measure atomic-scale and micro-scale changes occurring in samples subjected to identical reactive environmental conditions by incorporating a Raman Spectrometer into the ESTEM. We have used this correlative microscopy platform i) to measure the temperature from a 60 µm^2 area using Raman shifts, ii) to investigate light/matter interactions in plasmonic particles iii) to act as a heating source, iii) to perform concurrent optical and electron spectroscopies such as cathodoluminescence, electron energy-loss spectroscopy and Raman. We have developed an automatic image-processing scheme to measure atomic positions, within 0.015 nm uncertainty, from high-resolution images, to follow dynamic structural changes using a combination of algorithms publicly available and developed at NIST. This method has been proven to capture the crystal structure fluctuations in a catalyst nanoparticle during growth of single-walled carbon nanotube (SWCNT). Details of the design, function, and capabilities of the optical spectrum collection platform and image processing scheme will be presented.

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

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

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

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

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

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

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

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

We gratefully acknowledge financial support from the following agencies and grants: AFOSR FA9550-12-1-0268 (JL, PRI), AFOSR FA9550-12-1-0342 (CBE)), ONR N00014-13-1-0806 (JL, CBE), NSF DMR-1234096 (CBE), ONR N00014-15-1-2847 (JL) and N00014-16-3152 (JL).

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11:40am **NS+AS+EM+MI+SP+SS-ThM12 Single-Molecules Fluorescence Spectroscopy and Lifetime with Simultaneous Super-resolution Imaging for Materials Science Applications**

James Marr, CNST/NIST and University of Maryland, *M. Davanço*, CNST/NIST, *S.J. Stranick*, NIST, *B.R. Ilic*, *J.A. Liddle*, CNST/NIST

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

12:00pm **NS+AS+EM+MI+SP+SS-ThM13 Atomic Scale Surface Effects of Controlled Crystal Structure in III-V Semiconductor Nanowires: Preferential Surface Alloying and Local Electronic Properties.**

J. Knutsson, *M. Hjort*, Lund University, Sweden, *P. Kratzer*, University Duisburg-Essen, Germany, *J. Webb*, *S. Lehmann*, *K.D. Thelander*, Lund University, Sweden, *C.J. Palmstrom*, UCSB, *R. Timm*, ***Anders Mikkelsen***, Lund University, Sweden

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

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

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

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2D Materials Focus Topic
Room: 15 - Session 2D+AS+SS-ThA

Dopants, Defects, and Interfaces in 2D Materials
Moderator: Aubrey Hanbicki, Naval Research Laboratory

2:20pm **2D+AS+SS-ThA1 Electron Irradiation-induced Defects and Phase Transformations in Two-dimensional Inorganic Materials**, ***Arkady Krasheninnikov***, Helmholtz Zentrum Dresden-Rossendorf, Germany

Following isolation of a single sheet of graphene, many other 2D systems such as hexagonal BN, transition metal dichalcogenides (TMDs) and silica bilayers were manufactured. All these systems contain defects and impurities, which may govern the electronic and optical properties of these materials, calling upon the studies on defect properties. In my talk, I will present the results [1-6] of our first-principles theoretical studies of defects (native and irradiation-induced) in inorganic 2D systems obtained in collaboration with several experimental groups. I will further dwell on the signatures of defects in Raman spectra and discuss defect- and impurity-mediated engineering of the electronic structure of inorganic 2D materials. I will also present the results [7] of our theoretical studies of electron-beam induced phase transformations in 2D TMDs when electric charge, mechanical strain and vacancies are present. Based on the results of our calculations, we propose an explanation for this phenomenon which is likely promoted by charge redistribution in the TMD monolayer combined with vacancy formation due to electron beam and associated mechanical strain in the sample.

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2:40pm **2D+AS+SS-ThA2 Key Role of Rotated Domains in Oxygen Intercalation at Graphene on Ni(111)**, ***Luca Bignardi***, *P. Lacovig, M. Dalmiglio,* Elettra-Sincrotrone Trieste, Italy, *F. Orlando,* Paul Scherrer Institut (PSI), Switzerland, *A. Ghafari,* Helmholtz-Zentrum Berlin, Germany, *L. Petaccia,* Elettra-Sincrotrone Trieste, Italy, *A. Baraldi,* University of Trieste, Italy, *R. Larciprete,* Istituto dei Sistemi Complessi - CNR, Italy, *S. Lizzit*, Elettra-Sincrotrone Trieste, Italy

In this contribution I will provide a description of the oxygen intercalation at the strongly interacting graphene on Ni(111) and of the role of rotated graphene domains in triggering the intercalation. The system was studied by a combination of high-resolution x-ray photoelectron spectroscopy (HR-XPS), photoelectron diffraction (XPD) and angle-resolved photoemission (ARUPS) performed with synchrotron radiation. The HR-XPS measurements provided a full characterization of the interface at each stage of the intercalation, revealing the formation of an oxide layer between graphene and the metal substrate. The ARUPS data showed that the oxide layer efficiently decouples graphene from the substrate, restoring the Dirac cone and providing a slight n-doping. The C1s XPD measurements revealed that the graphene domains not aligned with the Ni substrate are the first to be intercalated with oxygen. At the same time, these domains are also preferential regions under which the oxygen is retained during the deintercalation process.

3:00pm **2D+AS+SS-ThA3 Atomic Structure of Defect and Dopants in 2D Semiconductor Monolayer MoS_2 and WS_2**, ***Jamie Warner***, University of Oxford, UK **INVITED**

Defects impact the properties of materials and understanding their atomic structure is critical to their interpretation and behaviour. I will discuss how aberration corrected TEM can be used to resolve the detailed structure of Sulfur vacancies and grain boundaries in CVD grown MoS2 and WS2. I will present our latest results on detecting single Cr and V impurity dopants that substitute Mo and W sites. Electron energy loss spectroscopy is used to map out the spatial position and confirm the contrast profiles from HAADF STEM images. Single Pt atimsnare added to the surface of MoS2 and we study the dynamics of hopping between S vacancies. finally I will discuss in situ observations of Pt nanocrystal formation on MoS2 using high temperature annealing.

4:00pm **2D+AS+SS-ThA6 Interaction of an Energetic Ar Molecular Cluster Beam with Graphene**, ***Songkil Kim***, *A.V. Ievlev, J. Jakowski, I. Vlassiouk, M.J. Burch, C.C. Brown, A. Belianinov, B.G. Sumpter, S. Jesse, O.S. Ovchinnikova*, Oak Ridge National Laboratory

Manipulation of low dimensional nanomaterials provides intriguing opportunities to design new functional materials as well as to develop next-generation device applications. To manipulate properties of low dimensional nanomaterials, extensive study has been conducted so far for interaction of energetic particles with low dimensional nanomaterials. However, most of the research has been focused on utilizing electron or light/heavy ion beams to study irradiation effects on alternation of structural, mechanical and electrical properties of nanomaterials. In this study, we investigated the effect of Argon molecular cluster beam irradiation on both defect formation and removal of organic contaminants on graphene. An Argon cluster beam was generated using the Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) combined with Atomic Force Microscopy (AFM). The ToF-SIMS allows for conducting in-situ monitoring of defect formation as well as organic contaminants removal. This leads to accomplishments of a high degree of controls over modification of graphene. A systematic study has been conducted to provide in-depth understanding about defect formation of graphene by synergistic theoretical and experimental approaches. Raman spectra clearly indicate that suspended graphene is more susceptible to Ar cluster beam irradiation than supported graphene on a SiO_2/Si substrate under the same irradiation conditions. The underlying mechanisms for the experimentally observed phenomena are demonstrated by theoretical analysis using the first-principles molecular dynamics calculations.

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

4:20pm **2D+AS+SS-ThA7 Efficient and Low-Damage N-doping of Graphene by Nitrogen Late-Afterglow Plasma Treatment**, ***Xavier Glad***, *G. Robert-Bigras, P. Levesque, R. Martel, L. Stafford*, Université de Montréal, Canada

Graphene already shows promises for the next generation of electronics and optoelectronics devices and other applications where a band gap or magnetic response is necessary [1]. The availability of versatile processing techniques is thus crucial to the development of these graphene-based technologies. An ideal and efficient nitrogen doping would precisely tune the N-doping and keep a minimal defect density. In this work, we explore the potential of the late afterglow of a microwave N_2 plasma at reduced pressure (6 Torr) for post-growth tuning of CVD-grown graphene films on copper foils.

A single graphene sample received five subsequent 30-second plasma treatments between which X-Ray photoelectron spectroscopy (XPS) and Raman spectroscopy (RS) were carried out. XPS measurements confirmed a strong N-incorporation increasing with the plasma treatment time (up to N/C = 29%) while RS assessed an uncommonly low damage generation (D/G ratio below 0.4) for such incorporation.

XPS, RS and ultraviolet photoelectron spectroscopy (UPS) were also performed on the sample after transfer to an Si/SiO_2 substrate via the PMMA method [2]. The results show a strong decrease of the N content (N/C = 6%) which is attributed to the desorption of out-of-plane adsorbed N due to the transfer. RS and UPS techniques both support an n-doping which is associated to the different aromatic N-incorporations deconvoluted from the high resolution XPS spectra.

The low ion density ($< 10^7$ cm^{-3}) and the high density of reactive neutral ($> 10^{14}$ cm^{-3}) and metastable species ($> 10^{10}$ cm^{-3}) of the nitrogen late-afterglow in our conditions [3] are believed to be the key of such efficient and low-defect N-incorporation in graphene.

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4:40pm **2D+AS+SS-ThA8 Exploring the Electronic Signature of Disordered Monolayer MoS_2**, ***Chinedu Ekuma***, *D. Gunlycke*, Naval Research Laboratory

Atomic defects in two-dimensional semiconductors could be used to induce insulator-metal- transitions (IMT), making it possible to have both insulating and metallic behavior in different regions of a single seamless material. Using a first-principles-based many-body typical medium dynamical cluster approach [1], we explore the electronic signature in monolayer MoS_2 resulting from atomic defects. Analyzing the typical (geometric) density of states, which unlike the arithmetic density of states, is able to discern localized and delocalized states, our calculations show a correlation-mediated IMT at the experimentally relevant sulfur vacancy concentration ~10^{13} cm^{-2}, depending on the strength of the intrinsic electron-electron interactions. We will also discuss the role of atomic defects on the absorption spectra.

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5:00pm **2D+AS+SS-ThA9 Heterogeneity in 2D Materials: From Localized Defects, Isoelectronic Doping to Macroscopic Heterostructures**, ***Kai Xiao***, *X. Li, M. Mahjouri-Samani, M.-W. Lin, L. Liang, A. Oyedele,* Oak Ridge National Laboratory, *M. Tian,* University of Tennessee, *A.A. Puretzky, J. Idrobe, M. Yoon, B.G. Sumpter,* Oak Ridge National Laboratory, *G. Duscher,* University of Tennessee, *C.M. Rouleau, D.B. Geohegan*, Oak Ridge National Laboratory **INVITED**

Two-dimensional (2D) materials are intrinsically heterogeneous, therefore controlling defects, understanding the impact of boundaries and interfaces, and developing means to exploit these heterogeneities is a transformative opportunity that could underpin future technologies and energy applications. This talk will discuss the fundamental understanding of the roles of heterogeneity, atomic interface, and disorder in 2D materials and their heterostructures. Through isoelectronic doping in monolayer of $MoSe_2$, the Se vacancies are effectively suppressed and photoluminescence is significantly enhanced due to the decrease of defect-mediated non-radiative recombination. In addition, we demonstrate the non-equilibrium, bottom-up synthesis of single crystalline monolayers of 2D $MoSe_{2-x}$ with controllable levels of Se vacancies far beyond intrinsic levels. Both substitutional dopants and vacancies were shown to significantly alter the carrier properties and transport characteristics within a single monolayer (e.g., n- to p-type conduction in W-doped $MoSe_2$ and in Se-deficient $MoSe_{2-x}$). The vertical and lateral 2D heterostructures by controlled assembly and doping will be discussed. In addition, the lattice misfit heterostructures of monolayer $GaSe/MoSe_2$ were synthesized by a two-step chemical vapor deposition (CVD) method. We find the vertically stacked $GaSe/MoSe_2$ heterostructures maintain vdW epitaxy with well-aligned lattice orientation between the two layers, forming an incommensurate moiré superlattice. The bottom up synthesis of 2D materials discussed here provides excellent control over the heterogeneity in 2D materials, which can tunably modulate the optical and electrical properties in 2D materials and their heterostructure.

Acknowledgment: Synthesis science was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences (BES), Materials Sciences and Engineering Division and characterizations were performed at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility

5:40pm **2D+AS+SS-ThA11 Evidence of a One-dimensional Metal in Twin-grain Boundaries of $MoSe_2$**, ***Horacio Coy Diaz***, *M. Batzill*, University of South Florida

In monolayer van der Waals-materials, grain boundaries become one-dimensional (1D) line defects. Here we show using angle resolved photoemission spectroscopy (ARPES) that twin-grain boundaries in the 2D semiconductor $MoSe_2$ exhibit parabolic metallic bands. The 1D nature is evident from a charge density wave transition, whose periodicity is given by k_F/p, where the Fermi momentum k_F is determined by ARPES. Most importantly, we provide evidence for spin- and charge-separation, the hallmark of 1D quantum liquids. ARPES shows that the spectral line splits into distinctive spinon and holon excitations whose dispersions exactly follow the energy-momentum dependence calculated by 1D Hubbard model, with suitable finite-range interactions. Our results also imply that quantum wires and junctions can be isolated in line defects in 2D materials, which may enable quantum transport measurements and devices.

Applied Surface Science Division
Room: 13 - Session AS+SS-ThA

Advances in Instrumentation and Data Analysis
Moderators: Thomas Grehl, ION-TOF GmbH, Germany, Bonnie June Tyler, Universität Münster

2:20pm **AS+SS-ThA1 Submicron Spot Sampling Resolution in Thermal Desorption Atomic Force Microscopy - Mass Spectrometry Via Rapid Heating Functions**, *S. Somnath, S. Jesse,* ***Gary Van Berkel***, *S.V. Kalinin, O.S. Ovchinnikova*, Oak Ridge National Laboratory

Atomic Force Microscopy (AFM) combined with Mass Spectrometry (MS) can provide the ability to map and correlate the molecular and physical properties of samples at sub-micron resolutions. One such hybrid system employs heated AFM probe for thermal desorption (TD) sampling of molecules from a surface and subsequent gas phase ionization and detection of the liberated species by MS. However, current heating techniques typically result in a minimum spot size of 1-2 µm for most real-world samples where the where the melting and vaporization points are further apart since the majority of the thermal energy from the thermal probe only melts or damages the substrate. While substantial research in the past has focused on improving the instrumentation, the waveforms used for heating thermal probes have been ignored. Heated AFM probes are capable self-heating at rates approaching 1E+9 K/s to reach temperatures in excess of 1300 K. Prior research has shown that increasing the heating rate (> 1E+9 K/s) can enable thermal desorption of intact molecules off the sample surface.

Here, we report on the use of voltage pulse trains to tailor probe heating such that spot sampling size was reduced and desorption efficiency (DE), defined as the ratio of the mass spectral signal to the volume of the desorption crater, was improved compared to the conventional heating method. We developed a 1D finite element joule-heating model of the probe-sample system that predicted the cantilever response to different heating functions, to guide the development and optimization of the heating functions and aid in interpreting experimental results. Using a model system composed of a thin film of ink containing pigment yellow 74 as a model system, desorption craters shrunk from 2 µm, using the conventional approach, to 310 nm using the optimum tailored heating function. This same pulsed heating function produced a 381× improvement in the DE and an 8× improvement in spatial resolution compared to the conventional heating approach showing that signal/amount of material sampled was improved significantly by this new probe heating strategy.

3:00pm **AS+SS-ThA3 Data Analysis in Thin Film Characterization: Learning More With Physical Models**, ***Lev Gelb***, *A.V. Walker*, University of Texas at Dallas **INVITED**

Chemical imaging methods, including imaging mass spectrometry (MS), are increasingly used for the analysis of samples ranging from biological tissues to electronic devices. Most chemical analyses for advanced materials, nanosystems, and thin films involve energetic beams of primary ions or electrons. These unavoidably cause chemical damage, including surface roughening, which confuses data interpretation. In secondary ion mass spectrometry (SIMS) matrix effects can be significant, in which the signal obtained from a given species may change depending on its surroundings. All these phenomena lead to the same issue: the data measured are not necessarily representative of the elements or species originally present, or their original locations. These effects can sometimes be exploited to provide new information or increased sensitivity, as in matrix-enhanced SIMS and the determination of overlayer thicknesses from attenuation of XPS substrate intensity.

We discuss analysis of such data using maximum *a posteriori* (MAP) reconstruction based on physically motivated models, and contrast this approach with statistical dimensionality-reduction techniques such as Principal Components Analysis. We present progress towards the quantitative extraction of chemical concentration profiles, component spectra, sample topography and other information from imaging mass spectrometry data in the presence of matrix effects. These include systems that demonstrate "weak" matrix effects, such as mixed self-assembled monolayers, and “strong” matrix effects such as those observed in ionic liquid matrix enhanced secondary ion mass spectrometry.

We also draw comparisons with related nonlinearities in other analysis methods, in particular X-ray photoelectron spectroscopy (XPS). While XPS is often considered to have linear response with concentration, this is only true under certain conditions and does not necessarily apply in sputter-based depth profiling experiments. We discuss extension of the MAP approach to such experiments and point out similarities with its application to SIMS data.

4:00pm **AS+SS-ThA6 Advanced Analysis of XPS and ToF-SIMS Data**, ***Matthew Linford***, *S. Chatterjee*, *B. Singh*, Brigham Young University, *N. Gallagher*, Eigenvector Inc., *M.H. Engelhard*, EMSL, Pacific Northwest National Laboratory **INVITED**

Surface analysis plays a critical role in many areas of science and industry, and X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) are much used analytical techniques that provide information about the outermost layers of materials. In this presentation, I discuss the application of multivariate spectral techniques, including principal component analysis (PCA) and multivariate curve resolution (MCR), to the analysis of XPS and ToF-SIMS depth profiles. Multivariate analyses often provide insight into data sets that is not easily obtained in a univariate fashion. The information content (IC) or entropy, which is based on Shannon's information theory, is also introduced. This approach is not the same as the mutual information/entropy approaches sometimes used in data processing. A discussion of the theory of each technique is presented. PCA, MCR, and IC are applied to four different data sets obtained via a ToF-SIMS depth profile through ca. 100 nm of C_3F_6 on Si, a ToF-SIMS depth profile through ca. 100 nm of PNIPAM (poly (N-isopropylacrylamide)) on Si, an XPS depth profile through a film of SiO_2 on Si, and an XPS depth profile through a film of Ta_2O_5 on Ta. PCA, MCR, and IC reveal the presence of interfaces in the films, and often indicate that the first few scans in the depth profiles are different from those that follow. Both IC and backward difference IC analysis provide this information in a straightforward fashion. Rises in the IC signal at interfaces suggest greater complexity to scans from interfaces in depth profiles. Results from PCA were often rather difficult to understand owing to the complexity of its scores and loadings plots. MCR analyses were generally more interpretable.

4:40pm **AS+SS-ThA8 Using the Auger D-Parameter to Identify Polyatomic Molecular Species**, ***Sabrina Tardio***, *P.J. Cumpson*, NEXUS, Newcastle University, UK

When analysing organic materials using XPS, the interpretation of the C1s spectra can be quite challenging and particularly difficult is to distinguish between unsaturated/aromatic carbon (hybridised sp2) and aliphatic carbon (hybridised sp3). This is because their binding energies of the two are very close and, in some cases, overlap or even invert the expected trend. This problem can be approached by observing the C*KLL* auger peak of the XPS spectra that is present around 260 eV of kinetic energy. Historically, information on the C sp2/sp3 ratio is obtained by analysing the width of this, extracting a metric commonly known as the D-Parameter. This is calculated by taking the first derivative of the auger feature and measuring the distance (in eV) between the position of the maximum (the most positive) and the minimum (the most negative) peaks observable. It was shown that there is a linear correlation between the D-Parameter with sp2 hybridised carbon content in a surface. For example, graphite (100% sp2 character) has a D-Parameter around 22eV while diamond (100% sp3 character) has a D-Parameter around 13eV. The D-Parameter is widely used for the identification of carbon allotropes; graphite, graphene, amorphous, diamond like carbon (DLC) diamond, hydrogenated diamond etc. However, the metric has found little or no use for the identification of unsaturated and saturated carbon in polymers or, more generally, polyatomic molecules. Although the principle remains the same; the correlation between D-parameter and sp2 carbon is still true, the presence of hydrogen as well as other atoms other than carbon, makes the relationship between the two much more complex. In this work correlations of the D-parameter with the C Sp2/sp3 ratio, the ratio between hydrogen bonded to C sp2 and sp3 and the ratio between heteroatoms (such as oxygen) bonded to sp2 and sp3 carbons is shown. In particular, a linear relationship between a combination of these ratios and the d-parameter was found. This allows one to predict the d-parameter for a given organic compound as well as to obtain more information about unknown species analysed. It will be shown how the combination of different information obtained from XPS spectra: photoelectron high-resolution peaks (C1s O1s), valence band and D-Parameter can lead to a quite accurate identification of organic molecules.

5:00pm **AS+SS-ThA9 XPS Analysis of Multilayer HfO_2 Using Hard and Soft X-rays**, ***Jennifer Mann***, Physical Electronics, *R. Inoue*, *H. Yamazui*, *K. Watanabe*, ULVAC-PHI, Japan, *J. Newman*, Physical Electronics

Hard x-rays can generally be considered as having photon energies > 5 keV, while photon energies below 5 keV are described as soft x-rays. Hard x-ray photoelectron spectroscopy (HAXPS) is typically performed at large synchrotron facilities, while most commercial lab-scale XPS instruments use soft x-rays. The PHI *Quantes* is a new commercial laboratory instrument equipped with two scanning microprobe, monochromated x-ray sources, Cr K_α (5414.9 eV) and Al K_α (1486.6 eV). Use of higher photon energies increases the mean free path of photoelectrons, resulting in an increased information depth obtained from the sample (~3x that of Al K_α). HAXPS measurements are therefore more sensitive to the bulk and contributions from the surface are minimized [1,2]. Toggling between x-ray sources allows non-destructive depth analysis of multilayer thin films and buried interfaces [1]. A more detailed description of the instrument will be presented in reference [3].

Initial analysis results on the high-k dielectric, HfO_2, obtained on the PHI *Quantes* using both hard and soft x-ray sources will be presented. Several samples of HfO_2 on SiO_2 on Si substrate with varying thicknesses of the HfO_2 and SiO_2 layers were analyzed. The HfO_2/SiO_2 thicknesses of the samples are as follows: 27Å/28Å, 80Å/22Å, 81Å/81Å and 263Å/22Å. Spectra were collected with a 90 degree take-off angle to maximize the information depth of each sample. As expected, the presence and relative intensities of SiO_2 and Si substrate peaks varied depending on the sample thickness, photon energy and photoelectron kinetic energy.

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5:20pm **AS+SS-ThA10 Novel Systems Toward Ambient Pressure Photoemission Spectroscopy**, ***Lukasz Walczak***, PREVAC, Poland

Nowadays, he complexity of materials and their surfaces is expanded across a wide range of topics, including surface science, catalysis, corrosion, photoelectrochemical energy conversion, battery technology, or energy-saving technologies [1-6]. An unique and exceedingly flexible analysis cluster with a detection system is needed for this applied research. Here the examples of innovative, compact ambient pressure X-ray spectroscopy systems with a some experimental results. One of the example will be a laboratory based high pressure x-ray photoelectron spectroscopy (HPXPS). The focus is on the usability of the system for various types of studies relevant for high level research for photo-catalytic reactions, light harvesting and solar cell development [6]. Further examples will be the advanced HP cell with the ambient pressure X ray spectroscopy system and flexible gas inlet system to allow for frontier research on gas-solid interactions. Systems are equipped with the possibility of process automatization in different environments. Additional it will be presented a spectrometer for the ambient pressure photoemission spectroscopy with a new monochromatic source, in order to permit complete characterization of the energy, angular, and later resolutions using different metal samples at different pressures.

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5:40pm **AS+SS-ThA11 Fabrication and Characterization of Heusler-Based Fe-Mn-Ge Epitaxial Films**, *B.D. Clark*, *N. Naghibolashrafi*, *S. Gupta*, *J. Jones*, *P.R. LeClair*, *A. Gupta*, ***Gary Mankey***, University of Alabama

Half metallic alloys have a wide range of applications such as spin filters, spin polarizers, and high signal giant magnetoresistive devices. The Heusler family of alloys is predicted to have a large number of half-metallic alloys. The MINT Center at UA maintains an extensive database of Heusler alloys (http://heusleralloys.mint.ua.edu/) to track and contribute to the application of Heuslers in technology applications. The formation of stable crystal structures that match theoretical predictions is one issue that we are addressing experimentally. In this work, high temperature magnetron sputtering is applied in an attempt to stabilize predicted phases. The sputtering system is confocal with four targets, so alloy composition can be controlled by carefully adjusting the power to separate magnetron guns containing elemental targets of Fe, Mn, and Ge. Both in-situ and ex-situ techniques are applied to evaluate the resulting films. For in-situ flux monitoring, a quartz crystal microbalance is used; for in-situ chemical analysis, Auger electron spectroscopy with a cylindrical mirror analyzer is performed; and for in-situ structural analysis, reflection high-energy electron diffraction is performed. The ex-situ techniques employed include x-ray reflectivity and diffraction, scanning transmission microscopy with selected area diffraction, energy dispersive x-ray analysis, and variable temperature magnetometry and transport. Our characterization results show that when deposited on sapphire, the full-Heusler Fe_2MnGe forms in the hexagonal DO_{19} crystal structure instead of the predicted $L2_1$ phase. The equiatomic half-Heusler alloy of FeMnGe forms in the $C1_b$ crystal structure when deposited on MgO(100). The results underline the importance of complete complimentary characterization techniques that include both chemical and structural analysis since the principle x-ray diffraction peaks of the $L2_1$ and $C1_b$ structures occur at the same locations. The two types of alloy films that were fabricated also exhibit markedly different magnetic behavior which will be discussed in detail.

We acknowledge MINT support through shared facilities. The work was supported by NSF DMREF Grant No. 1235396.

Biomaterial Interfaces Division
Room: 12 - Session BI+AS-ThA

Biomolecules and Biophysics at Interfaces
Moderators: Stephanie Allen, The University of Nottingham, UK, Markus Valtiner, TU Bergakademie Freiberg

2:20pm **BI+AS-ThA1 Engineering and Imaging Excitons for Brain Imaging of Modulatory Neurotransmitters**, *M. Landry*, ***Abraham Beyene***, University of California at Berkeley **INVITED**

For over 60 years, drugs that alter, mimic, or block modulatory neurotransmitters have formed the core arsenal for the treatment of neurological disorders such as depression, addiction, schizophrenia, anxiety, and Parkinson's disease. However, methods to diagnose and validate drug efficacy have remained largely the same: questionnaires and behavioral observations. The archaic nature of neurological disorder diagnosis results from the lack of tools to detect the molecular 'key players' of neuronal communication – the three primary modulatory neurotransmitters dopamine, serotonin, and norepinephrine. In this talk, we describe the design, characterization, and implementation of near-infrared optical sensors to image neurotransmitter dopamine. We show direct visualization of endogenous dopamine release over multiple rounds of acute brain slice stimulation, for over 80 minutes. We next introduce a new form of fluorescence microscopy for deep-brain neurotransmitter imaging: double infrared excitation-emission imaging. We characterize our findings in the context of their utility for high spatial and temporal neurotransmitter imaging in the brain, describe nanosensor exciton behavior from a molecular dynamics (MD) perspective, validate nanosensor use in vitro, and for nanosensor use in vivo, to correlate external stimuli (experiences, behavior) to chemical output (neurotransmission).

3:00pm **BI+AS-ThA3 Neurotrophin-like Peptides at the Interface with Gold Nanoparticles As New Nanoplatform for CNS Disorders**, ***Cristina Satriano***, *P. Di Pietro, N. Caporarello, C.D. Anfuso, G. Lupo*, University of Catania, Italy, *A. Magrì*, National Council of Research (IBB-CNR), Italy, *D. La Mendola*, University of Pisa, Italy, *E. Rizzarelli*, University of Catania, Italy

Neurotrophins are vital proteins for neural developing and maintenance as well as promising drugs in several neurodegenerative disorders.

In the present work we propose a combined approach of peptidomimetic and nanomedicine to tackle their current limits in an effective clinical application. Specifically, neurotrophin-mimicking peptides may allow for reducing some adverse side effects shown by the whole protein [1]. Moreover, the immobilisation of these peptides on nanoparticles offers many advantages, such as the protection against degradation, an enhanced permeability of barrier membranes and, if any, intrinsic nanomaterial therapeutic properties (for example, the anti-angiogenic and plasmonic features of gold nanoparticles, AuNPs) [2].

The functionalisation of spherical AuNPs of 12 nm of diameter by peptides owing respectively to the N-terminal domains of nerve growth factor, NGF1-14, and brain derived neurotrophic factor, BDNF1-12, were scrutinised both in the direct physisorption and in the lipid bilayer-mediated adsorption processes. UV-visible and X-ray photoelectron spectroscopies, QCM-D, dynamic light scattering, zeta potential analyses and atomic force microscopy were used to investigate the hybrid nano-biointerface. Both peptide- and lipid-dependant features were identified, in order to have a modulation in the nanoparticles peptide coverage as well as in the cellular uptake of NGF and BDNF peptides, as investigated by confocal microscopy. The promising potentialities in the capability to cross the blood brain barrier (BBB) were demonstrated with Human Brain Microvascular Endothelial Cells, a cell model representative of human brain endothelium that exhibits barrier properties comparable to other BBB models.

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4:00pm **BI+AS-ThA6 Controlling and Probing the Orientation of Immobilized Protein G B1 on Gold Nanoparticles Using Time of Flight Secondary Ion Mass Spectrometry and X-ray Photoelectron Spectroscopy**, ***Yung-Chen Wang***, *D.G. Castner*, University of Washington, Seattle

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

In this work, Protein G B1, a protein that can selectively bind to the Fc tail of IgG, was immobilized onto gold NPs (AuNPs) functionalized with maleimide and oligo-(ethylene glycol)(OEG) self-assembled monolayers (SAMs). Protein G B1 was immobilized onto AuNPs through specific maleimide-cysteine interaction. As the wild type Protein G B1 does not contain a cysteine, we can strategically introduce cysteine mutants on Protein G B1 to control the location of the maleimide-cysteine bonding. We used the surface sensitive analysis techniques of x-ray photoelectron spectroscopy (XPS) and time of flight-secondary ion mass spectrometry (ToF-SIMS) to characterize the surface elemental composition, coverage, and orientation of the protein G B1 immobilization process.

XPS analysis confirmed the AuNP functionalization with the maleimide SAMs. After incubation with protein containing cysteine mutant, the immobilization of the protein was demonstrated by the increased nitrogen signal on the surface of the AuNP. Wild type Protein G B1 cannot form the maleimid-cysteine bond and was effectively removed through conventional centrifugation-resuspension washes and dialysis cleaning.

ToF-SIMS analysis also confirmed the successful functionalization and protein immobilization on the AuNPs by identifying signature secondary ions of the maleimide functional group and amino acids. Utilizing the small sampling depth (~2nm) of ToF-SIMS relative to the size of Protein G B1 (~3nm), the orientation of immobilized protein G B1 was determined by comparing the ratio of secondary ion intensity originating from the opposite regions of the protein. Overall, site-specific maleimide-cysteine interaction and systematic surface characterizations enabled us to both control and probe the orientation of immobilized proteins on AuNPs. The systematic characterization of this study provided detailed information about protein-NP interactions and a platform for controlled immobilization for IgGs on NPs.

4:20pm **BI+AS-ThA7 Angiogenin Peptides and Gold Nanoparticles for Modulated Angiogenesis Processes**, *L.M. Cucci, C. Satriano, E. Rizzarelli*, University of Catania, Italy, ***Diego La Mendola***, University of Pisa, Italy

Angiogenin (Ang) is a physiological constituent of the human plasma and is a protein overexpressed in different types of tumours [1]. Gold nanoparticles (AuNPs) exhibit anti-angiogenic activity [2] and inhibit growth factor-mediated signalling *in vitro* as well as vascular endothelial growth factor (VEGF)-induced angiogenesis *in vivo* [3].

Herein, the fragment Ang60-68, including the putative cellular binding site of the protein Ang, has been synthesized and used to functionalize spherical AuNPs of 12 nm of diameter. The Ang mimicking activity of the peptide was evaluated by the staining of actin, a key target of the entire Ang, in terms of cell cytoskeleton reorganisation.

The hybrid peptide-nanoparticle assembly was obtained by physical adsorption of the peptides at the surface of AuNPs and was analysed by UV-visible spectroscopy, in order to characterise, with titration experiments, the variations of the plasmonic properties of AuNPs as well as the peptide spectral features. Another hybrid nanosystem was prepared by the immobilisation on AuNPs of the fluorescent analogous, Fam-Ang59-68, synthetized through an amidic bond which involved the N-terminal residue with the carboxyfluorescein (Fam) moiety.

The hydrodynamic size of the peptide-Au nanosystems was determined by dynamic light scattering (DLS) analysis.

Proof-of-work experiments with human neuroblastoma cells line were carried out to prove the non-toxicity of Ang-mimicking peptide functionalised gold nanoparticles. Furthermore, laser scanning confocal microscopy (LSM) images showed the localization of the peptide-nanoparticles at the cell membrane and their sub-cellular distribution. These data reveal an auspicious new platform for imaging and therapeutic activities in angiogenesis-involved diseases.

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5:00pm **BI+AS-ThA9 Exploiting Protein-Polyelectrolyte Interactions to Control and Tune Protein Immobilization at Interfaces. Applications in Biocatalysis and Separation Technology**, *C. Dupont-Gillain, A. Bratek-Skicki, **Aurélien vander Straeten***, UC Louvain, Belgium

INTRODUCTION: For many applications in biomedical science and biotechnology, it is challenging to control and tune the nature, amount, and activity of proteins at interfaces. Since proteins are polyampholytes, they do interact with polyelectrolytes (PE), in a way which strongly depends on the pH and ionic strength of the medium. It is usually considered that PE provide a mild environment to proteins, which may help keeping their activity unaffected by surface immobilization. Here, we explore two different approaches to take advantage of the PE-protein interactions for the controlled and tunable surface immobilization of proteins.

STRATEGY: In a first approach, mixed brushes of poly(ethylene oxide) (PEO), a protein-repellent polymer, and of a negatively- or positively-charged PE, respectively poly(acrylic acid) (PAA) and poly(2-(dimethylamine)ethylmethacrylate) (PDMAEMA), were prepared by the "grafting to" approach. These stimuli-responsive mixed brushes were used to selectively adsorb/desorb a given protein from a mixture of several proteins. In a second approach, PE-protein complexes were prepared then immobilized at interfaces within layer-by-layer (LbL) assemblies. This was in particular performed for PE-enzyme complexes, including PE-lysozyme and PE-glucose oxidase complexes. Systems including several enzymes were designed, with a view to further enable enzymatic cascades. Polymer brush formation and protein immobilization were monitored using quartz crystal microbalance, X-ray photoelectron spectroscopy and time-of-flight secondary ions mass spectrometry. Gel electrophoresis was used to determine the nature of proteins collected from the interface. PE-protein complex formation was assessed based on turbidimetry and dynamic light scattering measurements. Enzyme activity was measured based on standard assays.

RESULTS: (i) *Mixed polymer brushes-protein interactions*: From adsorption experiments with single and mixed solutions of albumin, lysozyme and fibrinogen on PAA/PEO and PDMAEMA/PEO brushes, it was demonstrated that the selective adsorption of one protein could be achieved, as well as the sequential desorption of these proteins when the three of them were adsorbed initially, by means of appropriate pH and I triggers. (ii) *PE-enzyme complexes as building blocks for LbL assembly*: PE-enzyme complexes were successfully built and characterized, then incorporated into LbL assemblies. The specific activity of lysozyme was higher when immobilized as a complex rather than in its native form.

CONCLUSION:The developed systems may find direct applications in separation technology, on the one hand, and in biocatalysis, on the other hand.

5:20pm **BI+AS-ThA10 Determination of Confined Molecular Structure by using X-ray-Surface Force Apparatus (XSFA) Study in Bio-interface Application**, ***Hsiu-Wei Cheng**, M. Valtiner*, Technical University Freiberg, Germany, *C. Merola,* Max-Planck Institute for Iron Research, Germany, *K. Schwenzfeier,* Technical University Freiberg, Germany, *M. Mezger, H. Weiss*, Max-Planck Institute for Polymer Research, Germany

In biology system, understanding of molecular dynamics at confined interface such as medicine diffusion across inter-cellular channel, lubrication at joints and electric signal transmission from nerves to nerves is boosting the modern medical and biomaterial study. To study the behavior of confined molecules in detail, a home-build X-ray surface force apparatus (XSFA) which combines a synchrotron X-ray with white light interferometry is used. In our first step, an imidazolium chloride based ionic liquid, which consists of a clear water induced phase change, was used as a modeling system to test the detection limit of XSFA. The result shows that the liquid phase change from liquid to liquid crystal can be clearly distinguished within a 50 to 100 nm confinement. Meanwhile, the application of X-ray reflectivity (XRR) reveal furthermore in-plane ordering information of the liquid crystal structure. Secondly, shear force were applied to study how confined liquids react to the friction to mimic the motion of joint. We found that friction behavior and molecular dynamics are strongly related to the gap size of the confinement, which is a useful information for artificial joint design. The combination of SFA and synchrotron X-ray has shown a great analytical potential to solve the interfacial molecular dynamic, which provides scientists another powerful tool to peer the world of molecule.

6:00pm **BI+AS-ThA12 Direct Quantification of the Hydrophobic-to-Hydrophilic Transition of Interaction Forces**, ***Laila Moreno Ostertag**, T. Utzig, P. Stock,* Max Planck Institute for Iron Research, Germany, *M. Valtiner*, TU Bergakademie Freiberg, Germany

When two surfaces come in close contact, several forces arise and, depending on the nature of the surfaces, these forces will show different magnitude. This principle may also be applied to diverse biological systems. Van der Waals forces have been on the radar for a century or so, and the identification of electrostatic interactions can be traced back to ancient times. It has also been clear that the behavior of such surfaces in terms of their polarity is associated to another type of force, called hydrophobic interactions.[1,2] The combination of these contributions leads to a better understanding of the interactions as the surfaces get closer together.

In this regard, we have revisited the hydrophobic interactions theory by studying the interaction forces between apposing symmetric surfaces of varying hydrophobicity via Atomic Force Microscopy and correlating them to the behavior of water at the interface. Short hydrophobic chains ending in either non-polar, hydrophobic groups or in charged heads and combinations of them were attached to smooth surfaces and tested under constant ionic force conditions. Mathematical modeling of the interactions was applied to the experimental results in order to obtain numerical parameters that are associated to the surface properties. Interesting results that are in apparent contradiction with the expected trend of the hydration parameters were found but can be explained by what we suggest is a breakdown of the water structure at the interface, which in turn can contribute to the understanding of attraction or repulsion between certain biological systems in aqueous media.

1. Hammer, M. U.; Anderson, T. H.; Chaimovich, A.; Shell, M. S.; Israelachvili, J., The search for the hydrophobic force law. *Faraday Discussions* **2010,***146* (0), 299-308.

2. Donaldson, S. H.; Røyne, A.; Kristiansen, K.; Rapp, M. V.; Das, S.; Gebbie, M. A.; Lee, D. W.; Stock, P.; Valtiner, M.; Israelachvili, J., Developing a General Interaction Potential for Hydrophobic and Hydrophilic Interactions. *Langmuir* **2015,***31* (7), 2051-2064.

Surface Science Division
Room: 25 - Session SS+AS+EM-ThA

Semiconductor Surfaces
Moderators: James Ohlhausen, Sandia National Laboratories, Petra Reinke, University of Virginia

2:20pm **SS+AS+EM-ThA1 Visualizing the Nanoscale Electrostatics of Material Interfaces**, ***Vincent LaBella***, SUNY Polytechnic Institute, *W. Nolting*, University at Albany, SUNY **INVITED**

Electrostatic barriers at material interfaces are the foundation of electronic and optoelectronic devices. Their nanoscale uniformity is of paramount concern with the continued scaling of devices into the sub 10 nm length scale and the development of futuristic nanoscale devices. This creates a fundamental and technological need for nanoscale insight into the fluctuations of electrostatic barriers at material interfaces. This presentation will focus on our development of visualizing the nanoscale electrostatic fluctuations that are occurring at metal-semiconductor and metal-insulator-semiconductor interfaces. This is accomplished by acquiring tens of thousands of ballistic electron emission microscopy spectra on a grid and fitting them to get the local Schottky barrier height. Both false color images as well as histograms of barrier heights are then created and compared to theoretical modeling. This has given new insight into both the scattering of the hot electrons and the interface composition and their effect on the electrostatics. For example, interfaces with incomplete silicide formation and mixed metal-species interfaces have been imaged and when combined with cross-sectional TEM provide new insight into their effects on the electrostatics that is not possible with conventional bulk transport measurements or other metrology techniques.

3:20pm **SS+AS+EM-ThA4 Reactions of Benzoquinone with Hydrogen Terminated Silicon Surfaces**, ***Meixi Chen**, J.H. Hack, A. Iyer, R.L. Opila,* University of Delaware

Iodine and Quinhydrone(QHY) dissolved in methanol have long been known to react with hydrogen terminated silicon surfaces to passivate electronic defects where photo-excited carriers recombine non-radiatively. The mechanism of this passivation is not well understood. The two constituent parts p-benzoquinone(BQ) and hydroquinone(HQ) have been studied separately in this work. We have shown that even though BQ and HQ are a redox couple, they behave very differently in reacting with silicon surfaces. The reaction is photolysis, pH sensitive and solvent-dependent. X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry were used to show that the BQ reacted with the surface. The electrical passivation of silicon surfaces is confirmed by carrier lifetime measurements where the silicon surface recombination velocity is deceased to 11cm/s. Changes in surface band bending are observed in XPS surface photovoltage. DFT calculations have also been performed. The reaction mechanism will be discussed in detail.

4:00pm **SS+AS+EM-ThA6 Uniform Reactivity and Bonding between Si(100) and GaAs(100) Wafers using Low Temperature (<180°C) Wet NanoBonding™ Optimized by Surface Energy Analysis**, ***Nicole Herbots***, *R. Islam*, Cactus Materials

Bonding two semiconductors surfaces such as Si and GaAs can increase performance in solar cell efficiency and high power electronics. In this work, the surface chemistry and topography of Si and GaAs are investigated to optimize the bonding of the pair. A new process called Nano-bonding™ [1,2] can nucleate cross-bonding molecules via electron exchange between two surfaces into a macroscopically continuous bonding "inter-phase" . The surfaces to be bonded are first chemically smoothed at the nano-scale and then terminated with matching "precursor phases". When activated, these phases exchange electrons. In other words, one surface is prepared so that it interacts preferentially with electron acceptors while the other surface is prepared to preferentially interact with electron donors. Hence, the precursor phases must be stable in air at room temperature until the surfaces are put into contact in clean-room class 10/ISO2 conditions and at low temperature (< 180°C). To bring the two surfaces into uniform contact while activating electron exchange and cross-bonding reactions, isotropic steam pressurization is applied, hence the name "Wet" Nano-Bonding™ [1,2].

The precursor phases are optimized based on insights provided by the Van Oss theory, combined with characterization of composition via Ion Beam Analysis (IBA), with surface energies via Three Liquids Contact Angle Analysis (3LCAA) and with surface topography using Atomic force Microscopy. On smooth surfaces, the Van-Oss theory separates contributions to the total surface energy γ^T into molecular interactions γ^{LW}, and interactions with electrons donors γ^+ and acceptors γ^-. These can then be each extracted accurately from 3LCAA measurements [2] using multiple (>3) drops. NanoBonding™ is observed when surface pairs complement each other for electron exchange: one surface with high γ^+ and the other with high γ^- leads to the formation of molecular cross-bonds. However, IBA and 3LCAA characterization results show that this criteria is not sufficient. The total surface energies γ^T for both GaAs, and Si must be larger than 40 mJ/m^2. This is due to the fact that the contribution of interactions with electron donors and acceptors needs to amount to at least 10-15% of γ^T, so that total surface interaction γ^T is not mostly controlled by molecular interactions γ^{LW} , but exhibits significant non-molecular interactions with both acceptors and donors. Only then can the dominance of interactions with acceptors on one surface and interaction with donors on the other surface promote NanoBonding™ effectively.

[1] Herbots N. et al. US Patent 9,018,077 (2015); 9,589,801 (2017).

4:20pm **SS+AS+EM-ThA7 Evaluation of Silicon Oxidation in Downstream Plasma Photoresist Strip with Reducing Chemistries**, ***Tongchuan Gao***, *V. Vaniapura*, Mattson Technology, Inc.

With the rapid development of ultra-shallow junction depth devices, minimized silicon surface damage with the photoresist (PR) strip processes is stringently required. Silicon oxidation associated with the strip processes results in silicon loss, and, therefore, adversely affects the source-to-drain current of the devices. This leads to an ongoing effort to develop strip processes with both high PR ash rate and low silicon oxidation rate. The commonly used PR removal technique, downstream oxidizing chemistry plasma, may result in significant silicon surface oxidation. Recently, reducing chemistry has been extensively investigated for PR stripping with very low silicon surface damage.

To understand the silicon oxidation behavior with PR removal using reducing chemistries, a series of experiments were conducted. Silicon wafers with controlled pre-processing native oxide thickness were treated in an inductively coupled plasma downstream reactor with different reducing chemistries. Processes with different reducing chemistry composition, plasma source power, processing time, and post-processing queuing time were systematically studied. Comparison was also made between reducing and oxidizing chemistries. The oxide growth was reduced by tuning the reducing chemistries as well as the hardware configuration. Ellipsometry and X-ray photoelectron spectroscopy (XPS) were used for oxide thickness measurement and quantitative chemical composition analysis for the pre- and post-processing wafers, respectively.

The experimental results demonstrated that higher H_2 content in the chemistry leads to more oxide growth, which may be attributed to that energized hydrogen species break the Si-Si bonds and then oxidation takes place, or that hydrogen can penetrate the silicon substrate and then are replaced by oxygen. Time-dependent oxidation tests showed that the oxide growth rate is higher for silicon wafers with thinner pre-processing native oxide layer due to the self-limiting nature of oxide growth. Most of the oxide growth happens within the first 30 seconds of the processes. PR ash rate and uniformity were monitored correspondingly to ensure satisfactory PR removal. Our work sheds light on the optimization of reducing chemistry plasma processes for efficient PR removal with minimal silicon oxidation.

4:40pm **SS+AS+EM-ThA8 Surface-sensitive Measurement of Dielectric Screening via Atom and Electron Manipulations**, ***Daejin Eom***, *E. Seo, J.-Y. Koo*, Korea Research Institute of Standards and Science, Republic of Korea

Dielectric screening is essential in determining semiconductor properties. Its assessment on the surface, however, is beyond the capability of conventional capacitance and optical techniques due to their lack of surface sensitivity. Here we present the surface-sensitive measurement of the dielectric screening by using the scanning tunneling microscopy and spectroscopy. To be specific, we generate a single-atom defect on the surface and vary its ionization state by a single-electron charge. We then assess in-plane dielectric constant and Debye length at the surface by probing the surface potential modulation with atomic resolutions. Such single-atom and single-electron manipulations on B δ-doped Si(111) surface unravel that the dielectric screening on this surface is much in excess of what the classical image-charge model predicts, which we ascribe to the strained bonds and the ionic character of the surface layers. Also, as an exemplary application of the measured screening parameters, we demonstrate determining the ionization state of a surface defect from the defect-induced band bending.

5:00pm **SS+AS+EM-ThA9 The Effects of UV Irradiation, Stage Temperature, and Radical Flux on UV-Ozone Treatment using High-aspect-Ratio Cave Structures**, ***Shogo Uehara***, *T. Sugawara, P. Wood*, SAMCO Inc.

UV-ozone treatment provides an atomic oxygen chemical reaction, where oxygen radicals are produced by UV-induced or thermal dissociation of ozone. Previously, it was found that ozone flux and stage temperature were critical for wettability improvement of polymer substrates such as polyetheretherketone (PEEK) [1]. However, in that study, the effects of UV irradiation, temperature, and oxygen radical flux were not clearly distinguished. In this research, a cave structure was employed to better elucidate the reaction mechanisms of UV irradiation, substrate temperature, and radical flux in UV-ozone treatment.

Polyimide-coated and photoresist-coated silicon coupons (5 mm x 5 mm) were placed at various depths inside a straight aluminum cave (6 mm x 6 mm square and 96 mm maximum depth). A SAMCO model UV-2 was used for this study. This system employs a cold cathode, mercury vapor UV lamp (185 nm and 254 nm), a remote (ex-situ) silent discharge high-concentration ozone generator (30-160 g/m^3) and sample stage heating (50 to 200°C). The surface wettability of polyimide was examined using the water contact angle, and the photoresist ashing rate was measured using a stylus profilometer (Ambios Technology, XP-200).

Generally, samples placed at higher aspect ratios showed higher contact angles and lower ashing rates. This indicated that the reactive species were deactivated or did not reach the sample when the aspect ratio became larger (i.e. the depth of the sample in the cave became greater). At an aspect ratio of 15, with ex-situ ozone only (no UV irradiation) and a stage temperature of 100°C, the polyimide samples did not show a significant ashing rate or contact angle decrease. However, at 200°C, the samples processed with ex-situ ozone only (no UV irradiation) showed contact angle of 15.40° against the initial value of 93.70° and an ashing rate of 9.95 nm/min. The samples processed using UV irradiation with ex-situ ozone at 200°C showed a contact angle of 75.93° and an ashing rate of 7.67 nm/min.

From these results, it was concluded that production of oxygen radicals was accelerated by thermal dissociation of ozone at the higher temperature. The oxygen radical flux produced at high temperature gradually decreased in the cave as the aspect ratio became greater, but it remained relatively high and caused temperature-driven surface chemical reactions. It was postulated that the 254 nm UV irradiation dissociated ozone that otherwise would have reached deep inside the cave and thermally dissociated [2].

[1] Uehara, S., Kawabe, T., Wood, P., & Tsuji, O. (2016). *MRS Advances*, **1**.11, 743-748.

[2] Wood, P., Wydeven, T., & Tsuji, O. (1993). *MRS Proceedings*, **315**. 237.

5:20pm **SS+AS+EM-ThA10 Density Functional Theory Study of the Effects of Surface Defects on the Interactions of Cl and α-Fe_2O_3 (0001) Surface**, ***Qin Pang***, *H. DorMohammadi, O.B. Isgor, L. Árnadóttir*, Oregon State University

Fe (III) oxides are the dominant structure of the outer layer of the iron passive film formed in alkaline environment, but chloride ions have been shown to induce depassivation of these passive films under the same conditions. Here we use hematite (α-Fe_2O_3) to represent the Fe (III) oxides and DFT+U method to investigate the mechanism of the depassivation by studying the interactions of Cl with both pristine α-Fe_2O_3 (0001) surface and the surface with defects. Total of four surfaces are considered, pristine surface, Fe vacancy surface, O vacancy surface and Fe-O pair vacancy surface. We found that the O vacancies have a positive effect on the adsorption of Cl on the surfaces while the Fe vacancy has a negative effect. The strength of the adsorption on the same site on the four surfaces can be ranked as O vacancy surface, Fe-O pair vacancy surface, pristine surface and Fe vacancy surface. The insertion of the Cl into the sub surface was studied on the four surfaces as well and was found to be endothermic for all four surfaces but surface defects have positive effects on the insertion of Cl by making it less endothermic. The insertion reaction is less endothermic on the O vacancy surface and Fe-O pair vacancy surface. On these two surfaces, the Cl insertion process goes through an O vacancy with reaction energy around 0.5 eV, which is about 1 eV lower than the reaction energy on the pristine surface. The Cl insertion energy is slightly coverage depended, but the insertion remains less favorable than the adsorption of Cl even at higher coverages.

Applied Surface Science Division
Room: Central Hall - Session AS-ThP

Applied Surface Science Poster Session

AS-ThP1 Depth Profiling Adventures in the Non-Semiconductor Chemical Industry, ***Kathryn Lloyd***, *J.R. Marsh*, DuPont

Until recently, technology development for SIMS depth profiling was centered around flat semiconductor wafers. Sputter rates could be determined using standards and doped standards. Experimental protocols continue to be optimized, but figures of merit are for the most part understood.

With the expansion of computer memory and disk space, sophisticated vendor and third-party software, and new cluster beam sputter sources, SIMS (specifically ToF-SIMS) depth profiling is now being applied to distinctly non-flat, standards-defying, or just structurally-complex systems. In the realm of inorganic depth profiling, the quasi-parallel spectral acquisition compared to quadrupole mass analyzers and the use of multivariate statistics can mitigate many problematic mass interferences. For organic/polymeric systems such as fibers, resins, and coatings, huge Argon gas cluster sputtering enables molecular detection of sub-surface species. Hybrid systems such as OLEDs and paints continue to present challenges because of the different sputtering conditions needed for the different layers. For all of these samples, the ability to visualize the depth profiling data in 3D graphics is very powerful.

One could argue that these experiments are less true "depth profiling" experiments and more "just sputtering" to obtain sub-surface chemical information. In any case, this presentation will show examples of sputtering ToF-SIMS applications in an industrial environment that have been made possible through the implementation of new Argon cluster sputter beams and/or the use of multivariate statistics.

AS-ThP2 High-energy Cluster Ions - Minimising Depth Profiling Artifacts for Solid-state Electrolytes, *J.D.P. Counsell*, Kratos Analytical Limited, UK, ***Chris Moffitt***, Kratos Analytical Ltd, *A.J. Pearse*, University of Maryland, College Park, *C.J. Blomfield, S.J. Coultas*, Kratos Analytical Limited, UK, *G. Rubloff*, University of Maryland, College Park

Classical lithium ion batteries rely on a liquid electrolyte however there have been significant developments towards replacing liquid electrolytes with solid state thin-films. Thin-film lithium ion batteries offer improved performance by having a higher average output voltage, lighter weights thus higher energy density, and longer cycling life than typical liquid electrolyte batteries [1]. In order to construct a thin film battery it is necessary to fabricate all the battery components, such as an anode, a solid electrolyte, a cathode and current leads into a multi-layered thin film. Lithium phosphorous oxynitride (LiPON) is widely used as the electrolyte in solid state micro-batteries due to low electronic conductivity, increased durability to cycling and ease of preparation.

Here we will use convention surface analysis techniques of XPS and sputter depth profiling to understand the surface and bulk chemistry of LiPON thin films formed via atomic-layer deposition (ALD) [2]. XPS yields quantitative information regarding the elemental composition of the near surface region to a depth of <10 nm. The elemental composition as a function of depth is probed and comparisons are made between conventional monatomic depth profiling and cluster depth profiling. We will also analyse complete battery stacks in their virgin and cycled states and discuss changes in elemental distributions at the interfaces between the electrodes and the solid electrolyte.

We demonstrate that the use of monatomic Ar ions is unsuitable for profiling materials with mobile light elements (Li) as the build-up of positive charge causes migration leading to erroneous depth composition. An alternative is proposed whereby the analyst uses 20 kV high-energy cluster ions in an attempt to mitigate the effects of ion migration and thereby improving confidence in the validity of the results.

[1] Y. Kato, S. Hori, T. Saito, K. Suzuki, M. Hirayama, A. Mitsui, M. Yonemura, H. Iba, R. Kanno, M. Armand, Nat. Energy 2016, 1, 16030.

[2] A. Kozen, A. Pearse, G. Rubloff, C-F Lin, M. Noked, Chem. Mater., 2015, **27**, 5324–5331

AS-ThP3 The Internal Composition and Structure of Fish Scales Investigated by ESCA and SEM, ***Gerry Hammer***, *S. Murcia, E. Lavoie, L.J. Gamble, D. Arola, D.G. Castner*, University of Washington

Fish scales are one example of a biological structure that provides physical protection without restricting the flexibility or mobility of the bearer. These types of structures are often complex composites and have attracted interest in the field of biomimetics, including the areas of personal armor and protective equipment. Elasmoid fish scales consist of mineral and organic materials, including hydroxyapatite, calcium carbonate and collagen fibers. Scales from pirarucu (*Arapaima gigas*), tarpon (*Megalops atlanticus*), and carp (*Cyprinus carpio*) were fixed, dehydrated, mounted in epoxy and microtomed to expose cross-sections. These sections were analyzed using ESCA and SEM to determine the composite structure and characterize the variations in composition through the scale thickness. ESCA images were obtained for a qualitative evaluation, and spectra from small area analyses provided information for a complementary quantitative analysis. The collagen fibers in the pirarucu were stacked in plys with a rotation angle of 90° between them, while in the tarpon and carp the rotation angle was 75° between successive plys. ESCA images and small area analyses showed the changes in composition between the mineralized limiting layer (LL), the mineral reinforced collagen fibers of the extenal elasmodine (EE) layer, and the collagen fibers of the internal elasmodine (IE) layer.

AS-ThP4 Ambient Pressure X-ray Photoelectron Spectroscopy of the III-V Semiconductor/Water Interface, ***Pitambar Sapkota***, *S. Ptasinska*, University of Notre Dame

Along with the intense study of semiconductors for promising photovoltaic application, these materials are also used for harvesting solar energy, where energy is stored in the form of chemical fuels. This is through photo-electrochemical (PEC) solar cells, which are being extensively explored recently. Performance and stability of such PEC devices largely depend on the electronic properties and chemistry at the interface of semiconductors and water. Oxidation of the semiconductor surface during operation has been shown to be the major cause of degradation in action and durability of such devices. This research has studied the interactions of water with the III-V semiconductor surface during operando condition using ambient pressure X-ray photoelectron spectroscopy (AP-XPS). The results obtained through this study help to determine the reaction pathway leading to oxidation and its extent on the surface. This knowledge can provide deeper insight into the tuning parameters necessary to obtain better operating and more lasting PEC devices.

AS-ThP5 Spectroscopic and Structural Studies of Iron Gall Ink, ***Karen Gaskell***, *A.A. Ponce*, University of Maryland, College Park, *L.B. Brostoff*, Library of Congress, *S.K. Gibbons*, *B. Eichhorn*, *P. Zavalij*, University of Maryland, College Park, *C. Viragh*, The Catholic University of America, *S. Alnemrat, J. Hooper*, Naval Postgraduate School at Monterey

Iron gall inks were the major writing medium from the middle ages through the 19th Century in the Middle East and Europe, and are present in hundreds of thousands of important cultural heritage objects worldwide, including books, manuscripts and artistic drawings. Iron gall ink depending on its preparation is well known for its potentially corrosive effect on paper or other writing medium, over time, changes in temperature and humidity can accelerate this degradation resulting in the worst case, complete loss of documents. The major ingredients of ion gall ink are iron salts, most often iron sulfate, tannic acids derived from vegetable sources such as gall nuts and gum arabic used as a binder. Despite much research in this area the chemistry of iron gall ink is still poorly understood. Through spectroscopic and structural measurements of synthesized model compounds and authentic documents combined with aging studies, we conclusively show that the main colorant of iron gall ink is an amorphous form of Fe(III) gallate$\cdot x H_2O$ ($x = \sim 1.5$–3.2). Comparisons between experimental samples and historical documents by XPS, Raman and IR spectroscopy, XRD, and Mössbauer spectroscopy confirm the relationship between the model and authentic samples.

AS-ThP7 Multicomponent Patterned Ultrathin Carbon Nanomembranes by Laser Ablation, ***Daniel Rhinow***, Max Planck Institute of Biophysics, Germany, *N. Frese*, Bielefeld University, Germany, *J. Scherr*, Goethe University Frankfurt, Germany, *A. Beyer*, Bielefeld University, Germany, *A. Terfort*, Goethe University Frankfurt, Germany, *A. Gölzhäuser*, Bielefeld University, Germany, *N. Hampp*, Philipps Universität Marburg, Germany

Carbon nanomembranes (CNMs) are two-dimensional materials obtained by electron beam-induced crosslinking of self-assembled aromatic precursors. Irradiation of aromatic SAMs with low-energy electrons leads to the formation of graphene-like molecular sheets with a thickness of only 1 nm. CNMs made from a single precursor molecule are in principle uniform. We have developed a method for the fabrication of internally patterned CNMs with locally varying chemical and physical properties. Photothermal patterning of SAMs enables the fabrication of arbitrary structured monolayers with lateral dimensions up to centimeters. We have used direct laser patterning to produce patterned aromatic SAMs, which were subsequently converted to CNMs by electron irradiation. Patterned CNMs have been analyzed by helium ion microscopy (HIM), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). Our experiments confirm that the structure of patterned CNM is preserved upon electron-induced crosslinking and transfer to different substrates.

AS-ThP8 Characterization of Laser-Treated Al-Alloy Surfaces

Harry Meyer, *D. Leonard, A. Sabau*, Oak Ridge National Laboratory

Lightweight materials, such as aluminum alloys, find increasing use in both automotive and aerospace applications. A key requirement for their use is effective surface cleaning and texturing techniques to improve the quality of the structural components. Work at ORNL focuses on the a novel surface treatment method using laser interferometry produced by two beams of a pulsed Nd:YAG laser. Operating at 10Hz of frequency, this technique has been used to clean aluminum surfaces, and at the same time creating periodic and rough surface structures. The influences of beam size, laser fluence, wavelength, and pulse number per spot are currently under investigation. Metallic aluminum is very reactive with atmospheric oxygen and quickly forms a native oxide surface layer. This layer of oxide on the surface can affect further manufacturing processes, such as welding, and must be removed prior to any joining step. Without proper surface preparation, seams and joints are susceptible to increased wear, degradation and, in some cases, catastrophic failure. There are many methods for removing aluminum surface oxides, including mechanical (i.e. abrasive wear) and chemical stripping, generally used for complex part geometries. Despite its effectiveness, chemical stripping also introduces higher costs associated with environmental protection and hazardous-waste management. Aluminum and aluminum alloy surfaces can be cleaned using high-energy laser pulses (nanoseconds to milliseconds range) and is accomplished mainly by surface melting and ablation. This method is a non-contact process without abrasion and chemical impact and the controllability offered by using lasers enables high-precision removal of surface oxides and other contaminants in the range from sub-micrometers to several millimeters. The process being optimized at ORNL is using a 2-beam method that not only cleans the surface for joining but textures the surface in a periodic manner. This poster present preliminary surface characterization results for the cleaning of Al-alloy surfaces. Results from optical and electron microscopies, scanning Auger microanalysis, x-ray photoelectron spectroscopy, and contact angle measurements on as received and laser–treated Al-2024 alloy surfaces will be shown. This abstract has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy.

AS-ThP11 Space Weathering Effects on Ceres: Novel Application of Surface Analytical Techniques to Questions in Planetary Science

Gerard Rodriguez Lopez, *C.A. Dukes, C. Bu*, University of Virginia, *L.A. McFadden*, NASA Goddard, *J-Y. Li*, Planetary Science Institute, *O. Ruesch*, NASA Goddard

Introduction: The solar wind plasma continuously streams from the Sun, interacting with the surfaces of airless bodies throughout the solar system. Sulfates, suggested by the thermal emission [1], and carbonates, identified by the 3.4 and 4.0 μm absorption features [2] on the surface of Ceres by NASA's Dawn spacecraft, will be exposed to solar wind H^+ and He^+ at ~1 keV/amu irradiation. We investigate the stability of these salts under 4 keV He^+ irradiation as solar-wind proxy at the low pressure/temperature conditions found in the Main Asteroid Belt.

Experiment: Anhydrous $MgSO_4$ and Na_2CO_3 powders are pressed into pellets and compositions are confirmed by X-ray diffraction. We measure diffuse optical reflectance prior and subsequent to irradiation through 0.2-2.5 μm (Lambda 1050) and 0.6-16 μm (Thermo Nicolet 670). Pellet samples are then introduced to ultra-high vacuum (10^{-9} Torr) and maintained at 110 K and effects of *in situ* 4 keV He^+ irradiation are monitored by X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy. Variations in surface composition and chemistry are identified and quantified as a function of fluence.

Results: Solar wind type ion irradiation of $MgSO_4$ damages the crystal structure, preferentially removing oxygen along with sulfur. XPS measurements imply the formation of MgO after $5\ x10^{17}\ He^+\ cm^{-2}$ (~15,000 years at 2.7 AU); a small shoulder on the sulfur peak suggests the presence of trapped SO_2, also confirmed by the IR feature observed at ~7.8 μm with irradiation. McCord et al. (2001) provides a potential decomposition pathway for $MgSO_4$ to SO_2 consistent with our observations. We observe secondary ion ejection (Mg^+, MgO^+, O^-, OH^-, H^-, S^-, and SO^-) from $MgSO_4$ with He-impact, and neutral spectra show loss of SO_2. Spectral darkening and reddening in the UV-Vis region is observed by *ex situ* optical spectroscopy after irradiation.

Bright Na_2CO_3 deposits darken as a function of solar wind exposure in the visible spectrum on a timescale of 1-10 thousand years. Visible darkening, caused by enhancement in surface Na as C and O are preferentially removed, can be completely reversed by exposure to H_2O vapor. For Ceres' bright regions, this suggests that brightest areas are likely to be the most recent material deposits or the most recently exposed to water.

Acknowledgements: We thank the NASA SSW and NSF-Astronomy programs. I thank Dr. Petra Reinke for her support and encouragement.

References: [1] Bu et al (2017) GRL (submitted) [2] Palumbo et al (2016)

LPSC 47, #2166 [3] Hapke et al (1981) Icarus 47, 361-367 [4] Hodyss et al LPSC 44,

#2328 [5] Lane (2007) Am. Mineral 92, 1-18 [6] McCord et al (2001) JGR 106, 3311-

3319.

AS-ThP13 Combustion Soot-derived Carbon Nanostructures: Microscopic and Spectroscopic Investigations

Ich Tran, *T. Aoki*, University of California, Irvine, *J. Beardslee, C. Moffitt*, Kratos Analytical, Inc.

The formation and fundamental properties of carbon nanostructures from combustion soot are investigated. Chemical and ultrasonic treatments were employed to extract elemental carbon nanostructures from raw soot obtained from combustions of biomass waste materials, as well as from ethylene flames. A combination of transmission electron microscopy and photoelectron spectroscopy/imaging techniques, was used to elucidate the relationships between the formation of combustion soot derived carbon nanostructures and their structural, chemical and electronic properties. These experimental data are correlated to models and mechanisms of soot formation and growth in combustion processes.

AS-ThP14 Probing the Chemical-State of Zinc centers in unknown Environments: A Comparison of Conventional and Core-core-core Auger Parameter Analyses

William Kaden, University of Central Florida

Citrus greening is a major problem for the agricultural community in the United States. Afflicted trees typically die within a few years of infection and produce fruit that is green, misshapen, and bitter to the taste. To mitigate the deleterious effects of this epidemic, a Florida-based team of researchers have developed a spray-dispersible bactericide known as Zinkicide^{TM}, which consists of zinc-containing nanoparticles capable of entering and freely traversing the phloem-containing vascular system of infected trees to selectively kill bacteria within infected cells. While controlling the size of the particles is of key importance to their membrane transverability, the chemical-state of the zinc centers is believed to be of key importance to controlling the resultant chemical interactions with the bacteria.

Having demonstrated proof-of-concept utility with laboratory-scale quantities of bactericides created from reagent-grade precursors, TradeMark Nitrogen has since begun scale-up efforts using agricultural-grade precursors. Given the importance of chemical-state on the bacteriacidal properties of the nanoparticulates, detailed characterization of the powders is of great importance. Unfortunately, traditional core-level XPS analysis of zinc centers is not sufficient for such characterization due to the relative insensitivity of the most intense transition (Zn 2p), which results in shifts too small to distinguish Zn in chemical compositions as disparate as Zn^0 and ZnO for example.

Due to this core-level insensitivity, most reported photoemission analysis of Zn makes use of an associated Auger transition to allow for Wagner plot comparisons to libraries of Zn in known compositions. Such analysis allows for peak assignments through both qualitative and quantitative comparisons with reference data, but is limited in its ability to disambiguate the chemical-states of Zn in environments not perfectly reproducing those of previously measured control samples due to the non-extrapolatable nature of Auger parameter measurements incorporating core-valence-valence transitions. By contrast, appropriately chosen combinations of core-level XPS and core-core-core Auger lines have been shown to provide more reliable estimates of final-state contributions to XPS peak shifts, thereby allowing for direct initial-state interpretation of those shifts (i.e. direct correlation between the extent of the final-state corrected XPS shifts and the degree of oxidation). In this talk, we will present XPS and Auger data sufficient to compare results from both types of analyses on both reference and various Zinkicide^{TM} samples made available for analysis by TradeMark Nitrogen.

Friday Morning, November 3, 2017

Applied Surface Science Division
Room: 13 - Session AS+MS-FrM

Unlocking the Sample History: Forensics and Failure Analysis
Moderators: Karen Gaskell, University of Maryland, College Park, Matthew Linford, Brigham Young University

8:20am **AS+MS-FrM1** ***In Situ* Diagnostics of the Coupled Mechanical and Electrochemical Degradation of High Capacity Electrode Materials in Lithium Ion Batteries**, ***Xingcheng Xiao***, General Motors R&D Center **INVITED**

Higher capacity in electrode materials (such as Silicon) is always accompanied by higher volume expansion. Most of the efforts to date in Si based electrodes have been focused on architectural design to avoid Si cracking. To achieve high current efficiency and long cycle life, the solid-electrolyte interface (SEI) must be mechanically and chemically stable despite the large volume-change. In this presentation, I will show you a comprehensive set of *in-situ* diagnostic techniques we developed to understand the coupled mechanical/chemical degradation of SEI layers during cycling. Based on the learning from the in-situ diagnostics, I will discuss some coating design strategies to achieve high cycle efficiency and extend the cycle life of high energy density batteries for electrical vehicle applications.

9:00am **AS+MS-FrM3 A Novel Approach to Characterizing the Silicon Anode Electrolyte Interface in Lithium Ion Batteries**, ***Caleb Stetson***, Colorado School of Mines, National Renewable Energy Laboratory, *C.S. Jiang, S. Harvey, K. Wood, G. Teeter, C. Ban, M. Al-Jassim*, National Renewable Energy Laboratory, *S. Pylypenko*, Colorado School of Mines

As the Lithium-ion battery (LIB) technology sector continues to develop, advances increasingly rely on innovative battery materials, particularly anode materials. Silicon has arisen as a frontier in anode material research mainly due to its high theoretical lithium capacity and the extensive knowledge regarding its processing and fabrication.

One of the principal challenges associated with the development of LIBs is the lack of understanding of the solid electrolyte interphase (SEI) layer that forms between the organic electrolyte and anode during the initial cycling of the battery. Formed from electrolyte decomposition products, this layer must be electronically insulating while still being permeable to lithium ions to allow for charge transport. This balance between differing properties is often difficult to maintain: if the SEI grows too thick, it loses its permeability to lithium; if it becomes too thin, the electronic resistance cannot be maintained and current will flow between the two electrodes. Measuring spatial variation in resistivity within this layer and correlating these data with chemical composition is of upmost importance to understanding SEI performance.

The SEI forms on the anode surface with thickness in the nanometer regime, which poses a challenge for finding the buried interface of the SEI with the Si anode. In order to locate and measure electronic properties at this interface, our group has utilized a scanning spreading resistance microscopy (SSRM) probe and scanner head to measure resistivity with nanometer-scale resolution. This system is installed in an argon glove box to minimize sample exposure to oxygen and humidity. The SSRM probe features a doped diamond-coated silicon probe that is both electronically conductive and wear resistant. The application of a sample-probe bias voltage while varying the force exerted on the probe in AFM contact mode allows for measurement of resistivity laterally and vertically.

Measurements of resistance vs. depth for SEIs demonstrate strong trends of resistance decrease as the probe penetrates deeper levels of the SEI. Several techniques are utilized to investigate the chemical composition at different depths of the SEI, including Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and X-ray Photoelectron Spectroscopy (XPS). Combining resistance and chemical speciation data originating from specific depths provides an interesting basis for the study of SEIs and the evolution of Si anodes under different cycling conditions with distinct electrolyte solutions.

9:20am **AS+MS-FrM4 In situ Liquid SIMS Investigation of Ion Solvation in Electrolytes for Lithium Ion Batteries**, ***Zihua Zhu***, *Y. Zhang, Z. Xu, M. Su, C. Wang, X.F. Yu, J.G. Wang*, Pacific Northwest National Laboratory

Ion-solvent interactions are of great fundamental and practical importance. However, many mysteries have long been existing in this field. For example, for the electrolytes used for Li ion batteries, preferential solvation and coordination number of a Li^+ ion are two interesting questions in hot debates so far. A major reason for above situation is lacking of reliable analysis techniques that can provide direct molecular information to elucidate ion-solvent interactions. In this work, in situ liquid SIMS was used to examine salt ion-solvent molecule interactions in several representative electrolytes used for Li ion batteries. Our data of the $LiPF_6$ in EC: DMC electrolyte show very strong molecular evidence that EC is preferentially solvated with Li^+, supporting previous ESI-MS and NMR results, but against recent Raman results. In addition, our data suggest that although the coordination number of a Li^+ ion can be as high as six in bulk electrolytes, three of them may be more stable than the remaining ones. In addition, it was observed that Li^+ and FSI^- ions tend to well-separated in 1.0 M LiFSI in DME electrolyte, consistent with our MD simulation results. As a comparison, many ion clusters were observed in the same concentration of $LiPF_6$ in EC: DMC electrolyte. The above findings suggest that in situ liquid SIMS can provide key evidence for better understanding of the ion-solvent interactions in the electrolytes for Li ion batteries.

9:40am **AS+MS-FrM5 Determining Bulk and Interface Chemical Damage Regimes in XPS Depth Profiling using Cluster Ion Beams**, ***Benjamin Schmidt***, *J. Newman, J.F. Moulder, J.E. Mann*, Physical Electronics

The development of gas cluster ion beams (GCIB) has provided fresh opportunities to study materials that exhibit chemical changes under monatomic argon ion bombardment during XPS surface cleaning or depth profiling. This is especially important as mixed inorganic/organic structures are increasingly used in applications such as OLED display devices and medical implants.

Several variables are available to fine tune cluster energy and size, which provides high levels of control to the user, but can present an overwhelming parameter space for practical use. For example, previous studies have shown that there is a relationship between the GCIB energy/atom and observed chemical changes. In the case of depth profiling bulk HfO_2, Barlow [1] observed that no change in Hf 4f peaks was detected for argon GCIB settings of 6 eV/atom, whereas a decrease to 2 eV/atom was required to minimize indium reduction in InAs. In a similar study on HfO_2, we observe similar results. By varying beam conditions, no Hf 4f reduction is observed at nominal 5.6 eV/atom, but is seen with an nominal 8 eV/atom beam. We discuss bulk and interface effects under these various conditions. For example, while no peak shape changes were observed in bulk HfO_2 at 5.6 eV/atom, reduced Hf oxide species are observed near the Si substrate, broadening the measured HfO_2/Si interface. We have investigated several other material systems, including polymers and Ti compounds, to provide guidance on general user settings.

[1] AJ Barlow, JF Portoles, PJ Cumpson. Observed damage during Argon gas cluster depth profiles of compound semiconductors. J App Phys 116, 054908 (2014)

10:00am **AS+MS-FrM6 In Situ Studies on Radiation Resistance of Nanoporous Metals**, ***Jin Li****, Texas A&M University, *C. Fan*, Purdue University, *Y. Chen*, Los Alamos National Laboratory, *X. Zhang*, Purdue University

High energy particle radiation induces severe microstructural damage in metallic materials. Void swelling is a general consequence of radiation damage and can drastically degrade the mechanical integrity of irradiated materials. Nanoporous (NP) materials have great potentials to alleviate irradiation-induced damage due to their giant surface-to-volume ratio. Here we show, by using in situ Kr ion irradiation of nanoporous Au in a transmission electron microscope, nanopores shrink during radiation, and their shrinkage rate is pore size dependent. In addition, from temperature-dependent studies, we found that both defect density and nanopores evolve with radiation temperature. Higher temperature results in lower defect density and reduced shrinkage rate of nanopores. The sink strength of nanopores as a function of temperature is estimated. Moreover, NP Au exhibits significantly enhanced swelling resistance compared to coarse-grained Au.

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* **ASSD Student Award Finalist**

This study sheds light on the design of radiation-tolerant nanoporous metallic materials.

10:20am **AS+MS-FrM7 Surface Analysis in the World of Fine Art**, ***Thomas Beebe, Jr.***, *Z. Voras, C. Goodwin, K. deGhetaldi, B. Baade, J. Mass*, University of Delaware **INVITED**

Connections between the science of surface analysis and the science of cultural heritage, such as it is, have been neither historically strong nor particularly productive, unfortunately for both fields. We are developing new collaborations aimed at changing this. Not all cultural heritage conservators adopt a scientific approach, and not all of those that do are willing to expand their scientific approaches to include surface-sensitive techniques such as XPS and TOF-SIMS, in many cases because their backgrounds have not led them to know about such methods. To be fair, we surface scientists don't have all the answers and often can't get them. Not all surface scientists are interested in pushing the boundaries of their sample types into such unconventional realms, and not all of those that are interested have the patience to develop the new sample-handling and sample-preparation techniques applicable to XPS and TOF-SIMS analysis, not to mention dealing with the ultra-small sample sizes of such precious works of art. This presentation will draw upon several recent examples from the speaker's research team to show how XPS and TOF-SIMS can be used to shed some light on mechanisms of chemical and physical degradation, proposed and applied methods of stopping such degradation, and proposed and applied methods of repairing such degradation. The examples will come from a range of paintings and other art objects spanning from the Italian Renaissance to the post-Modern era.

11:00am **AS+MS-FrM9 Surface Characterization of Acrylic Artists' Paints After Wet Cleaning with Water-in-Oil Microemulsions.**, ***Michael Clark***, *M. Keefe,* The Dow Chemical Company, *T. Learner,* The Getty Conservation Institute, *B. Ormsby,* Tate, UK, *A. Phenix,* The Getty Conservation Institute, *E. Willneff,* University of Leeds, UK

This paper reports on developments from collaboration between The Dow Chemical Company, Tate and the Getty Conservation Institute to improve cleaning systems for unvarnished modern painted surfaces. Increased use of new artistic paints since the 1950s has created a need for new cleaning approaches as traditional wet and dry cleaning systems have been found to be unsuitable in many cases.

This body of research has focused on the development of improved wet cleaning systems for artists' acrylic emulsion paints. The present study describes novel microemulsion systems based on water and mineral spirits, each formulated with different anionic or non-ionic surfactants. For this application, water-in-oil microemulsions were designed to capture the positive aspects of water-based cleaning systems (good pick-up and dispersion of soils; control over the conductivity and pH) while limiting, to a degree, the risks associated with exposure to aqueous cleaners. These notable cleaning solutions have been found to be very effective at removing surface soiling on acrylic paintings and other water sensitive works of art. A range of spectroscopic techniques have been employed to characterize the paint surface for changes induced treatment with different cleaning solutions. TOF-SIMS and XPS results show that trace amounts of surfactant residues from cleaning formulations remain on paint surfaces in some cases. Amounts vary depending on the surfactant type, inherent surfactant solubility, in addition to the clearance steps undertaken.

11:20am **AS+MS-FrM10 Surface and Depth Profiling of Soft Organic Thin Films. X-Ray Photoelectron Spectroscopy Study**, ***Tatyana Bendikov***, Weizmann Institute of Science, Israel, *S.J. Hutton,* Kratos Analytical Ltd, United Kingdom of Great Britain and Northern Ireland, *R. Balgley, G. de Ruiter, M. Lahav, M.E. Van der Boom*, Weizmann Institute of Science, Israel

X-ray Photoelectron Spectroscopy (XPS) is uniquely suited for the direct characterization of nanomaterials and thin films in terms of layer thicknesses, elemental composition and, frequently, the depth-distribution profile of elements across the film. In general, XPS is limited to probe the top <15 nm of a sample, and for thicker structures a digging-like etching process is needed.

Recent advances in depth profiling of organic and biological materials are based on sputtering with large Argon ion clusters (Ar_n^+).[1] Unlike monoatomic ions (Ar^+), large cluster ions do not penetrate deeply into the material, therefore sputter material from the near-surface region only, leaving the subsurface layers undisturbed and undestroyed.

Here we present two examples of successful XPS depth profiling of composite metal-organic architectures self assembled on the pyridine terminated silicon/ ITO substrates. The samples consist of four main components: metal complexes ($[M(mbpy\text{-}py)_3][PF_6]_2$, M = Ru (**1**) or Os (**2**); $Pd(PhCN)_2Cl_2$ (**3**) and (1,4-bis[2-(4-pyridyl)ethenyl]benzene, **BPEB**, (**4**) spacer molecules.

The first system was prepared by sequential immersion of the substrate in solution **1** (alternating with solution **3**) (4 layers) followed by **2** (alternating with **3**) (4 layers). Each layer is ~ 6 nm thick, thus the consequent total thickness of the organic film reaches 40-50 nm.[2]

In the second example molecular assemblies consist of different layers of metal complexes **1** and **2**, separated by repetitive spacers **4** alternated with **3**. Total thickness of the analyzed **[Ru-BPEB$_{12}$-Os]** assembly is ~20 nm.[3]

1. P. J. Cumpson et. al., *Surf. Interface Anal.*, **2013**,45, 1859-1868.

2. G. de Ruiter et. al., *J. Am. Chem. Soc.*, **2013**, 135, 16533-16544.

3. R. Balgley et. al., *J. Am. Chem. Soc.*, **2016**,138, 16398-16406.

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