Applied Surface Science Division
Room 204 - Session AS-MoM
Quantitative Surface Analysis

Moderators: Kateryna Artyushkova, University of New Mexico, Tim Nunney, Thermo Fisher Scientific, UK

8:20am **AS-MoM1 A Fistful of Data: The Good, the Bad and the Ugly of Quantitative Surface Analysis***, **Alexander Shard,*** National Physical Laboratory, UK **INVITED**

The properties of surfaces and interfaces govern the performance of most manufactured items, from advanced electronic devices, medical devices to packaging materials. The chemical analysis of such surfaces underpins the development of new products with better performance, ensures consistency in production and identifies the causes of failure. Commonly used methods, such as XPS and SIMS, can detect elements and chemical species, but also contain information on the amount of material and its distribution. This talk will describe the application of XPS and SIMS in the measurement of surface chemistry, highlighting the wealth of information available and the areas that need attention and development.

The measurement of coating thickness and the identification of defects is of major importance and will be a focus of attention. For thin (<10 nm) oxide films on silicon, XPS has been shown to be the most accurate method for such measurements and relies on a length scale that must be established by comparison with other methods. The applicability of XPS to other materials, non-planar samples and thicker films has improved in recent years and these developments will be described along with the potential use of both the inelastic background shape and HAXPES to extend the information depth, in some cases to more than 100 nm. The use of SIMS to measure surface composition is a particular priority, particularly in organic materials. Recent descriptions of matrix effects have highlighted the potential magnitude of this problem, but also point to methods to mitigate it. Although matrix effects are often taken into account when attempting to perform quantitative chemical analysis, their effects in SIMS images and depth profiles are often ignored but can be of overwhelming importance.

Recent international inter-laboratory studies have demonstrated that there can be significant disparity in the quantitative results reported by laboratories analysing the same materials using these techniques. The major causes of this variability will be discussed and shown to be predominantly due to the use, or misuse, of interpretational algorithms and reference data. The talk will highlight the role of ISO TC201 and VAMAS TWA2 in improving comparability and reproducibility in the results of these analytical methods.

9:00am **AS-MoM3 XPS and the Reproducibility Crisis***, **Donald Baer**, M.H. Engelhard,* Pacific Northwest National Laboratory

There is a growing awareness of reproducibility issues in many areas of science, including those associated with the AVS. In a 2016 survey of 1576 scientists reported in Nature (533 (2016) 452-454), 90% of those interviewed indicated that there was at least some level of reproducibility crisis in the scientific literature and more than half indicated that the crisis was significant. Data reproducibility and replication issues appear to be systemic and occur at multiple levels in the scientific process (in addition to fraud which is real but infrequent and not the focus here) including: i) within in a single study (Are results within one study appropriately reproducible, internally consistent, and adequately reported?), ii) within a laboratory (Have research groups established clear procedures and protocols to pass on to others the details needed for reproducing materials or other aspects of research?), iii) in reported results (Are measurement approaches and information in publications adequately detailed so that others could reproduce the work?). As the most commonly applied surface analysis method, use (or misuse) of XPS is a contributor to reproducibility issues but XPS is also an important tool that can be used to address some of the problems. Because of the high importance of the surface composition and chemistry on behaviors of materials as well as in biological and environmental systems, the use of XPS has been increasing for at least two decades. In the area of nanoparticles, lack of surface characterization is one source of material non-reproducibility. However, many researchers lack the experience or expertise needed to obtain the information sought from XPS measurements in useful and reproducible ways. Multiple types of problems appear and many of them can be observed in the literature including: analysis of samples at an inappropriate times or in non-optimal conditions; inappropriate handling and preparation of samples; damage to samples during analysis leading to faulty conclusions; incorrect or inconsistent quantification and/or spectral interpretation; lack of calibration and/or incorrect instrument set up; chemically meaningless fitting of data; inadequate reporting of methods, processes and results. This talk highlights examples of where XPS has been a tool for addressing reproducibility challenges, show a few examples of problem areas and summarize actions that the AVS is undertaking to help address reproducibility issues.

9:20am **AS-MoM4 Rapid Calculation Method of the Voigt Function for Use in the Analysis of Photoelectron Spectroscopic Data***, **Peter Sherwood,*** University of Washington

The basic shape of a photoelectron peak is Lorentzian, which is modified by instrumental and other factors, such as phonon broadening, to give a Gaussian contribution resulting in a peak shape that is a convolution of a Gaussian and a Lorentzian peak shape. The use of the correct peak shape is important in the analysis of photoelectron spectroscopic data. X-ray photoelectron spectra (XPS) from the core region often contain overlapping peaks which can be analyzed by fitting the experimental spectrum to a spectrum generated by the sum of a series of functions, each of which represent the individual peaks together with a background function.[1] XPS from the valence band region can be interpreted by calculating a spectrum from an appropriate model for the solid under study such as a band structure calculation, an approach which requires the inclusion of the photoelectron peak shape in order to correctly model the experimental spectrum.[2]

The Voigt function is a convolution of a Gaussian and Lorentzian and is the best representation for photoelectron peaks. Unfortunately the Voigt function cannot be represented directly as an analytical function and has to be evaluated numerically. Analytical functions were developed to approximate the Voigt function, and a number of so-called pseudo-Voigt functions have been developed. Analytical functions and their partial differentials can be calculated rapidly. One of the early pseudo-Voigt functions was a product function published by the author in 1979.[3]

The presentation will focus on how the true Voigt function can be rapidly calculated at speeds that are comparable to the calculation of pseudo-Voigt functions, with CPU times of a fraction of a second for complex curve fitting calculations on computers using Intel Core i7 processors.[4] The approach is based on the extensive work on the Voigt function by the atmospheric sciences community. Examples will be provided showing the application of the true Voigt function to the curve fitting of experimental core XPS data and the modelling of experimental valence band XPS data.

Reference

1.P.M.A. Sherwood, *J. Vacuum Sci. Technol.***1996**, *A14*, 1424.

2. P.M.A. Sherwood, *J. Vacuum Sci. Technol.***1997**, *A15*, 520.

3. R.O.Ansell,T.Dickinson,A.F.Povey,and P.M.A.Sherwood, *J. Electroanal. Chem.* **1979, *98***, 79.

4. P.M.A. Sherwood, *submitted for publication.*

9:40am **AS-MoM5 Statistical Analysis and Peak Fitting of X-ray Photoelectron Spectroscopy Data. Good Practices and Procedures for Working up this Information.***, **Matthew Richard Linford**, V. Jain,* Brigham Young University

Determining appropriate methods of peak fitting X-ray photoelectron spectroscopy (XPS) data remains an active area of research. In this talk we discuss some of our recent efforts to better understand and interpret XPS narrow and survey scans. These include a description and comparison of the Gaussian-Lorentzian sum (GLS) and product (GLP) functions and their use in XPS peak fitting. This discussion will include a description of the shapes of the GLS and GLP as a function of the mixing parameter in their definitions and a comparison of these functions to the Voigt function. We will also discuss uniqueness plots as used to identify fit parameter correlation, width functions for identifying changes in peak envelopes, and principal components analysis, multivariate curve resolution, and pattern recognition entropy for studying and comparing series/groups of spectra. Finally, we also hope to briefly mention the importance of other statistical tools for better understanding XPS peak fitting. These include using chi squared to compare fits, showing the residuals to identify poor fits and/or questionable parts of fits, showing the sum of the fit components as a comparison to the original spectra, and employing the Abbe criterion for identifying correlated residuals.

10:00am **AS-MoM6 Modeling the Shirley Background**, ***Alberto Herrera-Gomez***, *D. Mulato-Gomez,* Cinvestav-Unidad Queretaro, Mexico*; A.D. Dutoi,* University of the Pacific

In quantitative chemical studies employing X-ray photoelectron spectroscopy, the total background signal can be well described as the sum of two terms, one originated from inelastic electron-energy losses and another that is expounded by the empirical Shirley method [1,2]. The inelastic part is very well quantified by the Tougaard theory proposed in 1982 [3]; the Shirley part, in the near-peak region, can be quantified by the method illustrated by Proctor and Sherwood [4]. Since the Tougaard background meets the experimental signal at binding energies ~ 50 or 100 eV above the peak, the Shirley contribution must banish at those energies. Therefore, the Shirley signal begins as a step-like function at the peak position to then vanish at higher binding energies (examples of the Shirley-signal in the entire range will be presented).

We showed that the Shirley part of the background is related to the capture of photons by deeper levels [5]. The physical process can be described as interchannel coupling [6] but adding a strong involvement of the valence band, i.e., a process resembling off-resonant participator photoemission with the generation of a shake-off type signal. Based on this model, we will present an approximate method to estimate the Shirley signal in the near-peak region.

[1] 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.

[2] A. Herrera-Gomez et al. Practical methods for background subtraction in photoemission spectra, Surf. Interface Anal. 46 (2014) 897–905. doi:10.1002/sia.5453.

[3] S. Tougaard, P. Sigmund, Influence of elastic and inelastic scattering on energy spectra of electrons emitted from solids, Phys. Rev. B. 25 (1982) 4452–4466. doi:10.1103/PhysRevB.25.4452.

[4] A. Proctor, P. Sherwood, Data analysis techniques in x-ray photoelectron spectroscopy, Anal. Chem. (1982) 13–19.

[5] A. Herrera-Gomez et al., Intensity modulation of the Shirley background of the Cr 3p spectra with photon energies around the Cr 2p edge, Surf. Interface Anal. 50 (2018) 246–252. doi:10.1002/sia.6364.

[6] E.W.B. Dias, H.S. Chakraborty, P.C. Deshmukh, S.T. Manson, Breakdown of the Independent Particle Approximation in High-Energy Photoionization, Phys. Rev. B. 78 (1997) 4553–4556.

10:40am **AS-MoM8 XPS Spectra and Bonding In Ionic Transition Metal Compounds**, ***C. Richard Brundle***, C. R. Brundle and Associates*; P.S. Bagus,* University of North Texas

In previous work, [1-3] it has been shown that the cation 2p XPS can reflect the extent of the covalent bonding between the metal cation and the ligands in formally fully ionic TM compounds (ie a nominal "oxidation state"). In the present work, the dependence of the 3p XPS on the covalent character and the charge state of the cation is compared to 2p for selected oxides and halides. The objective is to determine the extent to which the 3p XPS can be used to identify the open shell occupation of the cation; i.e., the nominal oxidation state. It is also of concern to show how the covalent character of the compound modifies the 3p XPS from that for an ideal, isolated, atomic cation. The systems that have been examined include Mn and Fe oxides and halides which are compared with experiment, with each other, and with the calculated XPS of isolated Mn and Fe cations. For the theoretical results, ab initio wavefunctions, WF, have been determined and have been used to obtain the energies and intensities of the cation 2p and 3p XPS. The compounds are modelled with embedded clusters [4] and the WFs are solutions of the Dirac-Coulomb Hamiltonian. Implications for the limitations of quantitation, both elemental and chemical compound, using XPS peak intensities together with standards or theoretical cross-sections, are also discussed

1. C. J. Nelin, P. S. Bagus, C. R. Brundle, E. S. Ilton, and K. M. Rosso, J. Chem. Phys. (to be submitted).

2. P. Bagus, C. R. Brundle, and C. J. Nelin, J. Chem. Phys. (to be submitted).

3. P.Bagus, C. R. Brundle, and C. J. Nelin, presented at the AVS International Symposium, 2017

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

11:00am **AS-MoM9 Combinatorial Group XPS Analysis of Novel Material Systems**, ***Sarah Coultas***, Kratos Analytical Ltd, UK*; J.D.P. Counsell,* Kratos Analytical Limited, UK*; C. Moffitt,* Kratos Analytical Inc.*; C.J. Blomfield, A.J. Roberts,* Kratos Analytical Limited, UK

The combinatorial approach has been used widely to discover new material phases for many years now, allowing rapid exploration of composition–structure properties in complex material systems[1]. Compositional mapping is central to obtaining comprehensive pictures of material systems and mapping active chemical properties such as oxidation state and alloying as a function of composition is an integral part of understanding the underlying physical and chemical mechanism of the properties. Here we will apply the traditional approach of combinatorial techniques to explore several model systems using X-ray photoelectron spectroscopy XPS demonstrating the use of group analysis for two different application - ternary alloy formation post thin-film deposition and polymer microarray biomaterial screening.

Ternary metal compounds are used in a wide range of applications; as high-performance alloy materials and electronic semiconductors. We have examined a range of thin-films of first-row transition metals co-deposited on wafers to form a matrix of ternary alloys. The surface composition was analysed with XPS to determine the stoichiometric mixing for different alloy compositions and the extent of oxidation and chemical bond formation during deposition. Further analysis of large datasets allows the user to determine areas of particular interest and performance for further investigation – leading onto more detailed bulk/surface comparison studies using depth profiling techniques. Combinatorial methods will also be exploited for screening of functional biomaterials. The surface composition of a series of polymer microarrays are analysed with XPS to correlate differences in surface chemistry with specific biological performance. This high throughput method allows for library databases to be created for parallel screening of a wide range of polymer blends.

Workflow and data-handling will be discussed for the different systems as will illustrations and set analyses.

C. J. Long, J. Hattrick-Simpers, M. Murakima, R. C. Srivastava, I. Takeuchi, V.L. Karen and X. Li, *Rev. Sci. Inst.,* 78, 072217, 2007.

11:20am **AS-MoM10 Towards Spatially Resolved Quantification of Gold Nanoparticles Embedded in an Organic Matrix using Secondary Ion Mass Spectrometry**, ***Shin Muramoto***, *J. Bennett,* National Institute of Standards and Technology (NIST)

Secondary ion mass spectrometry (SIMS) has been successfully used to detect metal nanoparticles in a wide array of organic matrices such as in biological cells, tissue, and within polymer films. However, there are also instances when the nanoparticles cannot be detected at all, presumably due to a combination of charge competition with salts, sample charging, type of primary ion source, and ion dose density. For example, 150 nm Au nanoparticles (AuNPs) embedded in soil nematodes could easily be detected and resolved in a dynamic SIMS instrument using a Cs^+ ion source with a secondary ion yield of 10^{-12}, but no signal could be generated when a ToF-SIMS instrument equipped with a Bi_3^+ ion source was used, even when the sample was covered with a layer of Cs to enhance signal. To test what factors influence the ionization of AuNPs and to identify the ion dose density threshold for detection, a test sample was prepared through inkjet-printing of precisely measured amount of AuNPs onto porcine skin gelatin, a surrogate for biological tissue. By systematically changing the chemistry of the AuNP solution with solutes such as salts, it is possible to see their effect on nanoparticle ionization. The test sample can also be used for the quantification of nanoparticles by changing their concentrations, and see the effects of depth profiling in quantification by changing the distribution of nanoparticles in 3-dimensional space or position inside the film. The ultimate objective of this study is to create a test sample for the spatially resolved quantification of nanoparticles in a biologically relevant environment, to be able to quantify the number of particles in a given area without resorting to high lateral resolution instruments. The effort will also develop SIMS instrumentation into a tool that can be used for determining the pharmacokinetics and biodistribution of nanoparticles in tissue. Preliminary analysis using a ToF-SIMS instrument with a Bi_3^+ ion source showed that the mere presence of gelatin reduced the secondary ion yield of AuNPs by an order of magnitude. In addition, increasing the concentration of Na^+ from 10^{-6} M to 10^{-3} M led to a rather linear decrease in the secondary ion yield from 10^{-13} to 10^{-15}, consistent with the effect of salts on analyte response in an electrospray ionization system. [1] For the dynamic SIMS, the presence of gelatin had no noticeable effect on secondary ion yield of the nanoparticles.

[1] Constantopoulos, T. L.; Jackson, G. S.; Enke, C. G. Effects of Salt Concentration on Analyte Response using Electrospray Ionization Mass Spectrometry. 1999, , 625-634.

11:40am **AS-MoM11 Correction-Free Analysis of SIMS Data at High Mass Resolution in the Presence of Detector Saturation*, Lev Gelb*,** *A.V. Walker,* University of Texas at Dallas

We present a strategy for analyzing TOF SIMS data sets affected by detector saturation at high mass resolution. The detectors used in many instruments undercount ions due to saturation effects; if two or more ions arrive within a very short interval (the "dead time") only the first to arrive is recorded. This changes both the total number of ions collected and their statistical distribution. The dead time is typically short enough that only ions of the same nominal mass are affected, but a significant fraction of the total ions reaching the detector may still be missed; at low masses the great majority of ions often go undetected. Methods are available for "correcting" the collected spectra at both unit-mass and high-mass resolutions based on an assumed model for the behavior of the detector, but these are problematic when the number of scans taken is small and/or the saturation is sufficiently high. Calculation of the variance of the corrected data as required in many multivariate analysis techniques is also complex. As a result, performing quantitative analysis of TOF SIMS data while preserving high mass resolution remains problematic.

Rather than attempt to correct the measured data to remove saturation, we incorporate the detector behavior into the statistical distribution used in maximum *a posteriori* reconstruction, justified on Bayesian grounds. Essentially, this method finds the *most probably correct* spectra, given the observed data and available prior information. This approach has several advantages over previous techniques: no approximations are involved other than the assumed model of the detector, the method performs well even when applied to highly saturated and/or single-scan data sets, and it is possible to calculate uncertainty estimates for the extracted quantities. Our method is first demonstrated by application to individual spectra. The correctness of the approach and its efficacy are demonstrated on synthetic data sets, and then applied to selected experimental results. Performance on data of different degrees of saturation and/or total number of counts is determined and compared with existing correction-based approaches; the effects of dead-time duration on lineshape and FWHM are also explored. We then demonstrate extension of this approach to imaging data and compare and contrast the results obtained with analyses performed at unit-mass resolution.

Spectroscopic Ellipsometry Focus Topic
Room 202A - Session EL+AS+EM-MoM

Application of SE for the Characterization of Thin Films and Nanostructures

Moderators: Alain C. Diebold, SUNY Polytechnic Institute, Mathias Schubert, University of Nebraska-Lincoln

8:20am **EL+AS+EM-MoM1 Stealth Technology-based Terahertz Frequency-domain Ellipsometry*, Vanya Darakchieva,*** Linköping University, Sweden **INVITED**

We present the newly designed Terahertz (THz) frequency-domain spectroscopy (FDS) ellipsometer at the Terahertz Material Analysis Center (THeMAC) at Linköping university and demonstrate its application to a variety of technologically important materials and heterostructures. We show that employing concepts used in stealth technology for the instrument geometry and scattering anti-static coating, and modulation of the backward wave oscillator (BWO) THz source allows for effective suppression of standing waves enabling accurate ellipsometry measurements with high spectral resolution (of the order of MHz). We further demonstrate an etalon-based method for frequency calibration in THz FDS ellipsometry. The instrument can incorporate various sample compartments, such as a superconducting magnet, in-situ gas cells or resonant sample cavities, for example. Reflection and transmission ellipsometry measurements over a wide range of angles of incidence for isotropic (Si) and anisotropic (sapphire) bulk samples are presented together with determination of the material dielectric constants. We further demonstrate results from cavity enhanced THz optical Hall effect experiments on an AlGaN/GaN high electron mobility transistor structure (HEMT), determining the free charge carrier density, mobility and effective mass parameters of the 2D electron gas (2DEG) at room temperature. We show through in-situ experiments on epitaxial monolayer graphene exposed to different gases and humidities that THz FDS ellipsometry is capable of determining free charge carrier properties and following their changes upon variation of ambient conditions in atomically thin layers. Exciting perspectives of applying THz FDS ellipsometry for exploring low-energy excitation phenomena in condensed and soft matter, such as the vibrational, charge and spin transport properties of magnetic nanolaminates, polymers and hybrid structures for photovoltaics and organic electronics; and determination of THz optical constants and signatures of security and metamaterials are envisioned.

9:00am **EL+AS+EM-MoM3 Spectroscopic Ellipsometry and Finite Element Modeling based Optical Characterization of Highly Coherent Au-Si Slanted Columnar Periodic Nanostructures*, Ufuk Kilic,*** University of Nebraska-Lincoln*; A. Mock,* Linköping University, Sweden*; R. Feder,* Fraunhofer IMWS, Germany*; D. Sekora, M. Hilfiker, R. Korlacki, E. Schubert, C. Argyropoulos, M. Schubert,* University of Nebraska-Lincoln

An unprecedented and phenomenal control of anisotropic optical properties of a material is reported here by utilizing periodic arrangement of nanostructures. These artificially engineered structures exhibit distinct optical, mechanical, and magnetic properties when they are compared with their bulk counterparts which has recently gained a growing interest due to its potential applications in various optical and optoelectronic systems such as lenses, solar cells, photodetectors, and sensors [1-3]. In addition to the material choices (ie. elemental composition), the size and shape of these artificial structures also play a key role in tailoring the aforementioned inherent properties.

Unraveling the mechanisms that influence and control the optical properties of highly-porous, periodic, and three-dimensional arrangements of nanoplasmonic structures can offer new approaches for the development of next generation sensors. Glancing angle deposition and atomic layer deposition can be used to create periodic nanostructures with multiple constituent materials, so-called heterostructured metamaterials.[4] In this study, we employ a two-source (ie. Au and Si) electron-beam-evaporated, ultra-high-vacuum glancing angle deposition which allows for the fabrication of highly-ordered and spatially-coherent super-lattice type Au-Si slanted columnar heterostructured thin films. We perform a combinatorial spectroscopic generalized ellipsometry and finite-element method calculation analysis to determine anisotropic optical properties. We observe the occurrence of a strong locally enhanced dark quadrupole plasmonic resonance mode (bow-tie mode) in the vicinity of the gold junctions, with a tunable and geometry dependent frequency in the near-infrared spectral range. In addition, inter-band transition-like modes are observed in the visible to ultra-violet spectral regions. We demonstrate that changes in the index of refraction due to the concentration variation of a chemical substance environment (gaseous or liquid) within a porous nanoplasmonic structure can be detected by transmitted intensity alterations down to 1 ppm sensitivity.

References

[1] Kabashin, A. V., et al. Nature materials 8.11 (2009): 867.

[2] Schmidt, Daniel, and Mathias Schubert. Journal of Applied Physics 114.8 (2013): 083510.

[3] Frölich, Andreas, and Martin Wegener. Optical Materials Express 1.5 (2011): 883-889.

[4] Sekora, Derek, et al. Applied Surface Science 421 (2017): 783-787.

9:20am **EL+AS+EM-MoM4 Temperature Dependent Dielectric Function and Critical Point Comparison of bulk Ge and α-Sn on InSb*, Rigo Carrasco,*** *C. Emminger, N. Samarasingha, F. Abadizaman, S. Zollner,* New Mexico State University

Germanium is an indirect bandgap semiconductor with a bandgap of 1.55 µm at room temperature. Its band gap can be shifted to longer wavelengths and becomes direct by adding 5-20% Sn, which allows to detect efficiently in the IR range. Alloys of Ge and Sn are therefore of interest for photovoltaics, detectors and room temperature lasers (2-7 µm). Alpha-tin on the other hand, is a semimetal that, when under strain, has a very small band gap at the Gamma point of the Brillouin zone. We compare this direct band gap (E_0 peak) occurring in the infrared region of strained α-Sn on InSb to the absorption edge of Ge.

We investigate the temperature dependence of the complex dielectric function (DF) and interband critical points (CPs) of bulk Ge between 10 and 738 K using spectroscopic ellipsometry in the spectral range from 0.5 to 6.3 eV at a 70° angle of incidence [1]. The complex dielectric function at each temperature is fitted using a parametric oscillator model. Figure 1 shows that variations in temperature influence structures in the spectra of the DF. Furthermore, we analyze CPs in reciprocal space by studying Fourier coefficients as described in [2]. The peaks of the E_0 and $E_0+\Delta_0$ CPs are relatively narrow (Fig. 2) which makes the analysis of their broadenings difficult. A small excitonic peak is visible at the absorption edge E_0, also shown in Fig. 2.

Spectroscopic ellipsometry measurements were also performed on several epitaxially grown α-Sn layers on InSb in the spectral range of 0.03 to 6.5 eV. Comparing the results of the pseudo-dielectric function of Sn to the one of Ge shows a remarkable difference of both spectra in the IR- region, as demonstrated in Fig. 3. While structures at higher energies, such as the E_1 and $E_1+\Delta_1$ CPs, are similar in shape and amplitude for both materials, the E_0-peak in α-Sn is significantly larger than in Ge. Therefore, we believe that the E_0 peak in the spectrum of Sn is not due to excitons but can probably be explained by other parameters which influence the band structure, such as strain, composition, or free carrier concentration. The large peak between E_0 and E_1 is an interference fringe. We also compare the temperature dependence of the E_0 gap in Ge and alpha-tin.

This work was supported by the National Science Foundation (DMR-1505172) and by the Army Research Office (W911NF-14-1-0072). C. Emminger gratefully acknowledges support from the Marshallplan-Jubiläumsstiftung.

References

[1] C. Emminger, MS thesis (Johannes Kepler University, Linz, Austria).

[2] S. D. Yoo and D. E. Aspnes. J. Appl. Phys. **89**, 8183 (2001).

9:40am **EL+AS+EM-MoM5 Elastomer Thin Films and Conducting Nanostructures for Soft Electronics and Dielectric Elastomer Transducers***,* ***Bert Müller****, B. Osmani, T. Töpper,* University of Basel, Switzerland

Nanometer-thin polymer films are essential components of low-voltage dielectric elastomer transducers and will, for example, play a vital role in future artificial muscles [E. Fattorini et al.: Ann. Biomed. Eng. 44 (2016) 1355]. Organic molecular beam deposition (MBD) is a versatile technique to prepare silicone films under well-defined conditions [F. M. Weiss et al.: Mater. Design 105 (2016) 106; T. Töpper et al.: APL Mater. 4 (2016) 056101], but the achievable growth rates of about 1 µm per hour are too low for the fabrication of multi-layer devices. Therefore, we have developed electro-spraying as an alternative deposition method with one or two orders of magnitude faster rates [F. M. Weiss et al.: Adv. Electron. Mater. 2 (2016) 1500476; F. Weiss et al.: Langmuir 32 (2016) 3276]. For the two approaches, spectroscopic ellipsometry (SE) has been employed for in situ monitoring the film's optical properties, the film thickness and the surface morphology during deposition and ultra-violet (UV) light irradiation. The derived quantities were verified by means of atomic force microscopy (AFM). Subsequent to the silicone deposition and the cross-linking by UV light curing, Au has been deposited using MBD and sputtering. This deposition process was also quantitatively characterized using SE and controlled by means of the plasmonic fingerprints of the metal nanostructures [T. Töpper et al.: Adv. Electron. Mater. 3 (2017) 1700073]. The ex situ AFM measurements revealed well-known modulations characteristic for strained surface layers [B. Osmani et al.: Eur. J. Nanomed. 9 (2017) 69]. Recent nano-indentation tests have demonstrated that the Au-layers on the silicone near the critical stress regime hardly contribute to the overall elastic modulus and are, therefore, a sound basis for smart electrodes [B. Osmani et al.: Adv. Mater. Technol. 2 (2017) 1700105]. The nano-mechanical probing of the powered thin-film dielectric elastomer transducers evidenced the importance of the thickness homogeneity for such devices [B. Osmani et al.: Appl. Phys. Lett. 111, (2017) 093104]. The function of planar thin-film dielectric elastomer transducers can be precisely determined taking advantage of the cantilever bending approach [B. Osmani et al.: Rev. Sci. Instrum. 87 (2016) 053901]. Spectroscopic ellipsometry and advanced atomic force microscopy with nano-indentation capability enables us to thoroughly characterize the film morphology as well as the optical and local mechanical parameters of silicone and Au/silicone nanostructures.

10:00am **EL+AS+EM-MoM6 Spectroscopic Ellipsometry Investigation of Temperature Effects in Heated Self-organized 2D Arrays of Au Nanoparticles***,* ***Michele Magnozzi****, M. Ferrera, M. Canepa,* Università di Genova, Italy*; F. Bisio,* CNR-SPIN, Italy

Metal nanoparticles (NPs) have the interesting property of behaving as efficient converters of EM radiation into heat. While this can occur via interband photoexcitation, the presence of a Localized Surface Plasmon Resonance provides an extra degree of freedom to tune and optimize the heating [1].

Assessing the temperature of plasmonic NPs during or immediately after illumination is not an easy task, and typically involves the use of models that necessarily have to simplify the complex temperature-dependent dielectric and thermodynamic response of nanosystems; for this reason, a measurement of the T-dependent optical behavior of the NPs at well-defined, externally controlled T would greatly contribute towards a better understanding of the thermoplasmonic properties of metal NPs.

Spectroscopic ellipsometry (SE), being a high-sensitive and non-destructive technique, is an ideal tool to investigate the optical response of NPs systems, provided that a proper model is used for data analysis.

We report a T-dependent investigation of the optical response of densely-packed 2D arrays of gold nanoparticles supported on an insulating nanopatterned substrate [2]. SE measurements were acquired in the 245-1450 nm spectral range, under high-vacuum conditions and in the 25-350 °C temperature interval [3]. Using a dedicated effective medium approximation developed for this kind of systems [2], we are able to reproduce the complex anisotropic optical response of this system employing morphological parameters deduced by *ex-post* AFM analysis; the temperature-dependent dielectric functions of Au, required as input in the model, was obtained in a dedicated SE measurement. The model yields a very good agreement with experimental data at relatively low T; however, though the appropriate T-dependent dielectric function of Au is systematically employed, the model is no longer able to reproduce the data obtained at the highest T. Indeed, a satisfactory agreement is attained introducing an effective correction to the Drude term of the dielectric function of Au, that keeps into account morphological effects affecting the NPs surface - such as softening or melting - that enhance the surface electron scattering rate. Our analysis thus shows that the T-dependent optical properties of metal NPs deviate from simplified expectations, and validate SE as valuable tool to study the complex, anisotropic properties of plasmonic NPs systems.

References

[1] A.O. Govorov and H.H. Richardson. *Nano Today* 1:30-38, 2007

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[3] M. Magnozzi, F. Bisio, M. Canepa, *Appl. Surf. Sci*., 421:651-655, 2017

10:40am **EL+AS+EM-MoM8 Spectroscopic Ellipsometry of 2D WSe$_2$ Films***,* ***Baokun Song****, H.G. Gu, M.S. Fang,* Huazhong University of Science & Technology, China*; Y.L. Hong, W.C. Ren,* Shenyang National Laboratory for Materials Science Institute of Metal Research Chinese Academy of Sciences, China*; X.G. Chen, S.Y. Liu,* Huazhong University of Science & Technology, China

Recently, two-dimensional (2D) WSe$_2$ has become a popular choice for nanoelectronic, optoelectronic, and valleytronic devices due to its layer-modulated bandgap, high mobility ($\sim$200cm^{2}V^{-1}s^{-1}) and on-off ratio (10^8), and large spin-orbit coupling effect. The performance of those novel WSe$_2$-based devices strongly depends on the intrinsic optical properties of WSe$_2$, which exhibit an intriguing layer dependency. Therefore, the accurate and quantitative characterization of the layer-dependent optical properties of WSe$_2$ is essential to the optimal design of those related devices.

In this work, the dielectric function, bandgaps, and critical points (CPs) of WSe$_2$ ranging from monolayer to bulk have been comprehensively investigated and analyzed by spectroscopic ellipsometry over an ultra-broad band (0.73-6.42eV). The dielectric function of high-quality uniform WSe$_2$ specimens prepared by chemical vapor deposition were firstly obtained from the ellipsometric spectra. Then the bandgaps of the WSe$_2$ films were determined from their corresponding absorption coefficient spectra. We experimentally observed that the bandgaps of the WSe-$_2$ films change from 1.63eV in monolayer to 1.21eV in bulk. Moreover, by using the CPs analysis, a series CPs (A-H) in the dielectric function spectra were precisely distinguished and many of them were rarely reported before. The positions of CPs (A-E) exhibit an obvious red shift when the layer number increases, while the CPs (F-H) exhibit a slight blue shift. The former phenomenon can be partly interpreted as the decaying geometrical confinement of excitons, while the underlying reasons for the latter merit further studies. These novel and advanced optical features will promote the fundamental understanding of the electronic structures and the development of WSe$_2$-based devices.

11:00am **EL+AS+EM-MoM9 Thermal Evolution Process of $MaPbI_3$ Film Based on Spectroscopic Ellipsometry**, *X.Q. Wang, X.Y. Shan, H. Siddique, **Rucheng Dai**, Z.P. Wang, Z.J. Ding, Z.M. Zhang,* University of Science and Technology of China

Thermal Evolution Process of $MaPbI_3$ Film Based on Spectroscopic Ellipsometry

Xiangqi Wang, Xueyan Shan, Hassan Siddique, Rucheng Dai, Zhongping Wang, Zejun Ding, and Zengming Zhang*

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Abstract

During the last few years, the hybrid organic-inorganic methylammonium lead halide perovskite $CH_3NH_3PbI_3$ ($MaPbI_3$) has received great interest in the field of photovoltaics [1,2]. The relevant researches develop rapidly since the first realization of organic-inorganic hybrid solar cell, due to the excellent performance of $MaPbI_3$, such as high charge mobilities, suitable band gap and long carrier diffusion length. However the stability of MaPbI has been a key issue hinder the practical application [3]. Here we present in-situ spectroscopic ellipsomety measurement to understand the nature of thermal degradation process of MaPbI . The dynamic evolution process of dielectric constants of the as-prepared $MaPbI_3$ film through heating is obtained by an effective medium approximation model fitting. The proportion of $MaPbI_3$ and PbI is also obtained from the analysis of the ellipsometry data. The thickness of the film decrease in two-step, which is explained as the collapse of the PbI_2 frame. Our work provide the first in-situ detection of the optical properties through the degradation process of $MaPbI_3$ film, which can be consulted for further improving the stability of $MaPbI_3$.

References:

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2. J.Y. Jeng *et al*, $CH_3NH_3PbI_3$ Perovskite/Fullerene Planar-Heterojunction Hybrid Solar Cells, Advanced Materials 25, 3727-3732 (2013).
3. J.H. Noh *et al*, Chemical Management for Colorful, Efficient, and Stable Inorganic–Organic Hybrid Nanostructured Solar Cells, Nano Lett. 13, 1764-1769 (2013).

11:20am **EL+AS+EM-MoM10 a-Si as a Protective Layer to Block the Oxidization of Al mirrors**, ***Yhoshua Wug,*** University of California at Los Angeles*; D.D. Allred, R.S. Turley,* Brigham Young University

Arguably, the best path to produce a truly broadband, e.g., an IR-optical-UV-EUV (extreme ultraviolet) mirror, for a future space observatory is an EUV multilayer mirror coated by a very thin bare aluminum layer. However, using a bare Al layer presents challenges that first must be overcome. Al oxidizes rapidly when contact with the atmosphere occurs. The customary solution is to cover the mirror with a protective evaporated fluoride layer. Unfortunately, these are opaque under ~110 nm, whereas, bare Al itself is highly reflective down to 85nm and could be used as a mirror to that wavelength if a barrier were not required. Once the mirror is in space far from the Earth, where there is no oxygen, Al would no longer need a barrier layer. Could a barrier be removed in space? Neither fluorides nor aluminum oxide can be removed once they are deposited without damaging the mirror's surface and destroying VUV reflectance. a-Si could be used as a protective layer that is potentially removable without roughening the Al surface. Dry hydrogen etching processes exist that could remove a silicon barrier as silane gas which would dissipate quickly in space. Such a process would use the Al layer as an etch stopping barrier in removing the a-Si protective layer. But is a-Si a suitable barrier for Al? We report our variable-angle spectroscopic ellipsometry studies of evaporated a-Si thin films on evaporated Al films. We discuss the conditions where a-Si can act as a protective layer to block aluminum oxidation.

11:40am **EL+AS+EM-MoM11 Terahertz to Mid-infrared Dielectric Response of Poly-methacrylates for Stereolithographic Single Layer Assembly**, *D.B. Fullager, **Serang Park**, Y. Li, J. Reese,* University of North Carolina at Charlotte*; E. Sharma, S. Lee,* Harris Corporation*; S. Schöche, C.M. Herzinger,* J.A. Woollam Co. Inc*; G.D. Boreman, T. Hofmann,* University of North Carolina at Charlotte

Producing THz optical components with arbitrary shapes using additive manufacturing is receiving considerable interest because it offers a rapid, low-cost avenue for THz imaging system development. In order to design such THz optical components appropriately, accurate knowledge of the complex dielectric function of the materials used for stereolithographic 3D fabrication, is crucial. In this presentation we report on the complex dielectric function of several poly-methacrylates which are frequently used for stereolithographic fabrication. Spectroscopic ellipsometry data sets from the THz to mid-infrared spectral range were obtained from isotropically cross-linked poly-methacrylate samples. The data sets were analyzed using stratified layer optical model calculations using parameterized model dielectric functions. While the infrared spectral range is dominated by several strong absorption features with Gaussian profiles, these materials are found to exhibit only weak absorption in the THz range. In conclusion we find that thin transmissive THz optics can be easily achieved using poly-methacrylate-based stereolithographic fabrication. Possible origins of the observed absorption in the THz spectral range are identified and pathways to reduce it are discussed.

Industrial Physics Forum
Room 101B - Session IPF+AS+BI+NS-MoM

Biofabrication: From Tissue to Organ

Moderators: Jason Bardi, American Institute of Physics, Jim Hollenhorst, Agilent Technologies

8:20am **IPF+AS+BI+NS-MoM1 Strategic Thinking on the Architecture and Design of Scaffolds for Regenerative Medicine**, ***Buddy D. Ratner,*** University of Washington, Seattle **INVITED**

Scaffolds for use in medicine and biology might be traced back to the 1940's when parachute cloth was first used for vascular prostheses. However, in the mid-1980's scaffolds took off as an essential tool in tissue engineering. This talk will explore some of the basic biology of porosities, roughness and textures on cell responses in vitro and tissue responses in vivo. University of Washington studies will be presented demonstrating enhanced healing and regeneration with precision control of pore structures for in vivo applications. The use of surface techniques and tools will be addressed for decorating the surfaces of scaffolds with biological molecules. Finally, the potential of secondary ion mass spectrometry (SIMS) for analyzing and imaging pore structure will be addressed.

9:00am **IPF+AS+BI+NS-MoM3 Sequential Bottom-up Assembly of Synthetic Cells**, ***Joachim Spatz,*** Max Planck Institute for Medical Research, Germany **INVITED**

The evolution of cellular compartments for spatially and temporally controlled assembly of biological processes became an essential step in developing life. Synthetic approaches towards cellular-like compartments are still lacking well-controlled functionalities as would be needed for more complex synthetic cells. In part, this is due to the mechanical and chemical instabilities of the lipid-based protocells and a lack of technical means for their well-controlled manipulation. We developed droplet supported lipid bilayer vesicles by microfluidics to generate mechanically and chemically stable and, therefore, manipulable cell-like compartments with a well-defined chemical and biophysical microenvironment. The enhanced stability enabled the sequential loading of such compartments with biomolecules by pico-injection microfluidics without compromising their functionality as synthetic cells. We demonstrate a successful sequential bottom-up assembly of a compartment with lipids, transmembrane proteins (integrin, F_oF_1-ATP synthase) and cytoskeleton proteins which would not assemble in a fully functional way by mixing and including them in one pot at once

9:40am **IPF+AS+BI+NS-MoM5 Activation of Inkjet Printed Cells Enhances Microvasculature Formation in Host Tissues**, ***Thomas Boland**, B. Oropeza, L.H. Solis,* University of Texas at El Paso*; M. Yanez,* University of South Carolina **INVITED**

Bioprinting refers to the co-deposition of cells alongside scaffolding materials to build two- and three-dimensional constructs for tissue engineering applications. 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. Studies of membrane properties of thermal inkjet printed cells by evaluating showed normal electrophysiology, but short-term membrane disruptions, which allow small molecular weight molecules to enter. Cell viability was high and apoptotic behavior was not upregulated. Alginate (1%) and gelatin type B (2.5%) constructs or scaffolds were prepared by bioprinting of a crosslinker with endothelial and endothelial / β cells. Control scaffolds were manually pipetted with the same cells and without any cells.Upon implantation the bioprinted endothelial cell constructs showed a nearly ten-fold increase in blood vessels was observed (p= 0.009), a dose response was observed but the β cells seemed to inhibit vessel formation. The explanted implants show large complete vascular features on the H&E and CD31 stains; Immunohistochemistry showed the tissue were regenerated with the human cells that made up a large part of the vasculature. Further insights into how the inkjet printing process activated endothelial cells will be presented. Understanding these processes will improve bioprinting and may eventually lead to creating fully vascularized large soft tissues, which have not been successfully grown thus far.

10:40am **IPF+AS+BI+NS-MoM8 Challenges in Organ-specific Vascular Engineering and Tissue Assembly***, **Ying Zheng**,* University of Washington **INVITED**

Engineered tissues have emerged as promising new approaches to repair damaged tissues as well as to provide useful platforms for drug testing and disease modeling. Outstanding challenges remain in 1) the lack of well-defined and mature cell sources to facilitate translational outcomes and 2) the lack of control over vascular structure and perfusion efficiency in engineered 3D tissue constructs, preventing large-scale tissue fabrication, and leading to insufficient perfusion after implantation in vivo. In this talk, I will present recent progress in my lab in engineering microvasculature from human pluripotent stem cell derived endothelial cells, and their anastomosis *in vitro* and infarcted heart *in vivo*. The eventual goal of this drive is to use the single cell source to derive organ-specific vascular cells and tissue for regeneration. Next I will discuss our work in understanding the human microvascular endothelial cell heterogeneity from four major organs, heart, lung, liver and kidney and describe their distinct structure and function. I will show an example of using human kidney-specific microvascular cells to model kidney specific injury. Finally I will discuss challenges and future perspectives towards engineering human organ-specific tissue models.

11:20am **IPF+AS+BI+NS-MoM10 Bioprinting for Translational Applications: *The Quest for Whole Organ Fabrication, James J. Yoo,*** Wake Forest School of Medicine **INVITED**

Tissue engineering and regenerative medicine has emerged as an innovative scientific field that focuses on developing new approaches to repairing cells, tissues and organs. Over the years, various engineering strategies have been developed to build functional tissues and organs for clinical applications. However, challenges still exist in developing complex tissue systems. In recent years, 3D bioprinting has emerged as an innovative tool that enables rapid construction of complex 3D tissue structures with precision and reproducibility. This developing field promises to revolutionize the field of medicine addressing the dire need for tissues and organs suitable for surgical reconstruction. In this session novel and versatile approaches to building tissue structures using 3D printing technology will be discussed. Clinical perspectives unique to 3D printed structures will also be discussed.

In-situ Microscopy, Spectroscopy, and Microfluidics Focus Topic
Room 202B - Session MM+AS+NS+PC-MoM

Mechanical, Electrical, Thermal and Optical Systems for In situ TEM (9:00-10:100 am)/Beam Induced Effects and Processing in Liquid/Gas Cells for TEM/SEM (10:40-11:40 am)

Moderators: Suneel Kodambaka, University of California, Los Angeles, Olga Ovchinnikova, Oak Ridge National Laboratory

9:00am **MM+AS+NS+PC-MoM3 Cantilever Substrates for Quantitative Growth Experiments in the Environmental Transmission Electron Microscope***, **Frances Ross**,* IBM T. J. Watson Research Center, MIT **INVITED**

Environmental TEM is an excellent tool for obtaining quantitative information on growth processes and materials transformations. However, it is essential to measure the local temperature, pressure, and other key conditions at the sample location. Well controlled and accurately calibrated *in situ* experiments often make use of specially designed samples and involve various methods for direct measurement of the reaction parameters. Here we describe some of these strategies, but focus on one particular sample design which we suggest is well suited for experiments addressing chemical vapor deposition. In this sample design, growth takes place at the tip of a hairpin cantilever microfabricated from single crystal silicon and heated by direct current. Epitaxial growth is possible on the cantilever surfaces, and deposition on materials such as amorphous silicon nitride is achieved by first coating the cantilever. We discuss how the local temperature and pressure can be measured by monitoring a calibrated growth process. We also discuss how growth can be examined under more complex environments, such as electric fields, using designs involving multiple cantilevers and actuators. We finally discuss approaches to higher pressure than is possible in conventional ETEM by integrating cantilevers in a closed gas cell. Custom substrates based on microfabricated designs appear poised to expand the possibilities of quantitative *in situ* growth experiments to exciting new regimes and materials systems.

9:40am **MM+AS+NS+PC-MoM5 In Situ Laser Heating and Excitation in the Transmission Electron Microscope: Recrystallization, Grain Growth, Phase Separation and Dewetting in $Ag_{0.5}Ni_{0.5}$ Thin Films***, **Philip D. Rack**,* University of Tennessee Knoxville*; Y. Wu,* University of Notre Dame*; C. Liu,* University of Tennessee Knoxville*; T.M. Moore, G.A. Magel,* Waviks Inc.*; D. Garfinkel,* University of Tennessee Knoxville*; J.P. Camden,* University of Notre Dame*; M.G. Stanford, G. Duscher,* University of Tennessee Knoxville

Motivated by the desire to image excited state and high temperature materials phenomena at the nano and atomic scale, Waviks Inc. has recently developed an in situ optical delivery tool for the (scanning) transmission electron microscope (S)TEM. The tool used in these experiments contains two optical delivery channels and is mounted on a Zeiss Libra 200 (S)TEM system. A 785 nm wavelength laser diode system coupled through a 5 µm mode field diameter single-mode fiber is used to deliver >200 mW to the sample surface. The laser can be gated from a few ns to continuous wave (cw) at repetition rates up to 16 MHz. A second optical channel with a 100 µm core diameter broad spectrum multimode fiber is also available for coupling to any excitation source in the wavelength range from 200 to 2100 nm using a standard SMA fiber connector. The system is mounted to a 3 axis (+/- *x,y,z*) nanomanipulator for focusing to the electron/sample coincident point (with sample tilted at ~45 degrees). The system contains a lens system to re-image the fiber optics (1x) at a working distance of ~10 mm, which is long enough eliminate charging and minimizes re-deposition of material. To demonstrate the functionality of the tool, we will show photothermal annealing results of a supersaturated $Ag_{0.5}Ni_{0.5}$ film. We will demonstrate recrystallization, grain growth, phase separation and solid state dewetting of the films via various laser powers, pulse widths, pulse numbers, laser radius. Finally, we will demonstrate interesting in situ excited state phenomena via electron energy gain spectroscopy of plasmonic silver nanoparticles.

10:00am **MM+AS+NS+PC-MoM6 In situ Transmission Electron Microscopy Study of the Mechanical and Electrical Properties of Single III-V Semiconductor Nanowires***, **Lunjie Zeng**,* Chalmers University of Technology, Gothenburg, Sweden*; C. Gammer,* Austrian Academy of Sciences, Austria*; B. Ozdol,* Lawrence Berkeley National Laboratory*; T. Nordqvist, P. Krogstrup,* University of Copenhagen, Denmark*; A.M. Minor,* Lawrence Berkeley National Laboratory*; W. Jäger, E. Olsson,* Chalmers University of Technology, Gothenburg, Sweden

III-V semiconductor nanowires possess outstanding electronic and mechanical properties that can be utilized in future high-speed electronic devices, solar cells and sensors. To better understand these properties and their relations to the microscopic structure of the nanowires, it is critical to directly correlate the structure and properties of single nanowires. However, the direct characterization of the mechanical and electrical properties of single nanowires, in particular, the correlation between them is still a challenge. In this study, we directly investigate the intrinsic mechanical and electromechanical properties of individual InAs nanowires using in situ transmission electron microscopy (TEM).

Quantitative stress, strain and electrical transport measurements were carried out on single InAs nanowires simultaneously. A Hysitron PI95 nanoindentation TEM holder was used for the in situ TEM study. By using an electrical push-to-pull (EPTP) device in the in situ TEM holder, tensile stress was applied via the nanoindenter in the holder while the force applied on the nanowire was measured by a transducer in the holder. The EPTP device also enables current-voltage (I-V) measurements on single nanowires. Nanoscale lattice strain mapping within the nanowire was performed using scanning transmission electron microscopy (STEM) combined with nanobeam electron diffraction (NBED). NBED diffraction patterns were acquired using a Gatan K2 direct detection camera. Based on the detailed strain and stress measurements, Young's modulus and Poisson's ratio of single InAs nanwires were directly determined. The

Young's modulus of single InAs nanowire is smaller than that of the bulk, while the Poisson's ratio of the InAs nanowire is similar as the bulk InAs. The electrical measurements showed that the resistivity of the InAs nanowires decreased continuously with increasing tensile stress. The piezoresistance coefficient of the nanowire was found to be significantly larger than that of bulk InAs. Moreover, significant inhomogeneous strain distribution within the nanowire under stress was unveiled by STEM-NBED strain mapping. The inhomogeneous strain distribution at nanometer scale can increase the resistivity of the nanowire by enhancing electron scattering. The findings demonstrate unique mechanical and electromechanical properties of the nanoscale InAs wires and provide new insights of the correlation between mechanical strain and electrical transport properties in free-standing nanostructures.

Financial support from Swedish Research Council and Nanoscience and Nanotechnology Area of Advance at Chalmers University of Technology are acknowledged.

10:40am **MM+AS+NS+PC-MoM8 Radiolytic Synthesis of Nanostructured Materials using *In situ* Liquid Cell Microscopy***, **Raymond Unocic**, X. Sang, A. Belianinov, O.S. Ovchinnikova, K. More, S. Jesse,* Oak Ridge National Laboratory **INVITED**

There are a wide range of solution-based strategies available for the size- and shape-controlled synthesis of functional nanomaterials for applications in catalysis, energy storage, biomedical, optical, and electronics. To elucidate growth mechanisms, *in situ* liquid scanning transmission electron microscopy (STEM) plays a role for directly imaging and quantifying growth dynamics of nanoparticles from liquid-phase precursors. In this work, we report several strategies for the *active* controlled synthesis of metallic and bimetallic nanoscale architectures using the concept of radiolytic synthesis. In one approach, we developed a direct-write, template-free method to fabricate self-supporting, hollow, metallic nanostructures, and we interpret the formation mechanisms based on direct observations of nucleation and growth. The electron beam used for imaging stimulates radiolysis, promoting the dissociation of water (H_2O) molecules and the formation of complex radical species such as aqueous electrons (e_{aq}^-) and other reducing and oxidizing species. The highly reducing radiolytic species assist in the chemical reduction of metal ions from the precursor solution, resulting in the formation of a metallic nanocrystal seed, which then acts as a catalyst for H_2 gas generation forming a metal encapsulated hollow nanobubble. In another approach, a custom-built electron beam nanopositioning and scan-generator system is used to precisely control the position and electron dose of the focused electron or ion beam to fabricate metallic and bimetallic nanostructured materials. These strategies enable fundamental electron beam interaction studies and open a new pathway for direct-write nanolithography from liquid-phase solutions.

This research was supported by the Center for Nanophase Materials Sciences, which is a United States Department of Energy Office of Science User Facility.

11:20am **MM+AS+NS+PC-MoM10 Electron Beam Induced Cross-Linking in Liquid Hydrogels***, **Tanya Gupta**, A. Kolmakov,* National Institute of Standards and Technology (NIST)

Advances in additive manufacturing of bio-friendly polymeric materials over the last decade has revolutionized the diverse fields like rapid prototyping, tissue engineering, drug delivery etc. The technology currently relies on laser, thermal or UV induced 3D printing. Other triggers with similar effects can in principle be used as ionizing radiation to carry out the crosslinking. In this work we explore the use of electron beam to perform 3-D patterning at mesoscale and explore its potential towards rapid prototyping. In particular, knowledge of electron interaction with the printing ink allows us to predict effect of various control parameters like beam energy , current and dwell time on the topology of the features formed. A Monte-Carlo simulation coupled with a rigorous kinetic model is built to study the interplay of dose distribution, total interaction volume and diffusional effects of the active radiolytic species.

11:40am **MM+AS+NS+PC-MoM11 Nanoscale Chemical Reactor Based on Localized Surface Plasmon Energy in Environmental Transmission Electron Microscope***, **Canhui Wang**[1], W.-C. Yang,* UMD/NIST*; R. Sharma,* National Institute of Standards and Technology

Miniaturizing chemical processes in a research context has many advantages, including the ability to examine the reaction at atomic resolution, the reduced usage of costly and/or hazardous chemical reagents, and the ability to be integrated into analytical devices. [1-2] However, the current efforts of miniaturizing chemical processes have been limited by achievable minimum reaction volume and the lack of precision control over the reaction locations. Herein, we demonstrate a nanoscale chemical reactor utilizing localized surface plasmon (LSP) resonance as the energy source in an environmental transmission electron microscope (ETEM). This approach allows us to confine the reaction within proximity of the nanoparticle while taking advantage of the high spatial resolution capability of the electron microscope to monitor the reaction.

Plasmonic nanoparticles, such as Au or Al, are placed in a reactive environment inside the ETEM. The composition and partial pressure of the gases are controlled by a gas handling system. Electron energy-loss spectra (EELS) imaging is used to acquire both elemental and LSP maps from the same nanoparticle. This allows the mapping and quantification of different gas adsorption on the nanoparticle surface. The energy required for the reaction of interest is provided by the LSP resonance excited by the high energy electron beam. The reaction location is confined within proximity of the nanoparticle due to the local field enhancement of the LSP resonance. Using a non-negative matrix factorization machine learning algorithm [3], we map the energy transfer pathways from the electron beam to the nanoparticle at nanometer spatial resolution and 0.08 eV energy resolution. The temperature distribution of the nanoparticle is monitored with few-nanometer spatial resolution using time-resolved EELS. Reaction processes, including morphological changes and transition of crystalline phases, are monitored using aberration-corrected atomic-resolution movies. By utilizing LSP resonance to initiate the reaction, we show that chemical processes can be confined in a nanometer scale volume, and modulated by electron flux. Important factors of the reaction, including composition of the reactants, adsorption of gases, transfer of energy, change of temperature, as well as reaction dynamics, can be monitored with nanometer or atomic resolution. Our approach paves the way to understanding a wide range of chemical reactions at the atomic scale.

References:

[1] Abdelgawad, Mohamed, et al. Lab on a Chip 9.8 (2009): 1046-1051.

[2] Williamson, M. J., et al. Nature materials 2.8 (2003): 532.

[3] O. Nicoletti, et al. Nature 502.7469 (2013): 80.

Plasma Science and Technology Division
Room 104A - Session PS+AS+EM+SS-MoM

Plasma-Surface Interactions

Moderator: Yohei Ishii, Hitachi High Technologies America Inc.

8:20am **PS+AS+EM+SS-MoM1 Atomic-scale Numerical Simulation of a Nanometer-Scale Hole Etching of SiO2 with a Carbon Mask***, **Charisse Marie Cagomoc**, M. Isobe, S. Hamaguchi,* Osaka University, Japan

The current generation of mass-produced semiconductor devices uses nanometer-scale technologies to fit millions of transistors in a single chip. However, the demand for higher integration density is still increasing. For example, sub-10 nanometer transistors have been already established for experimental devices, and fabrication technologies of such devices for mass production are now being developed. For nanometer-scale fabrication processes, the granularity of the structure reflecting the finiteness of atomic sizes and the stochasticity of atomic motion may play important roles in determining the final structure. In this study, to understand such atomic-scale effects in nano-scale fabrication processes, we performed molecular dynamics (MD) simulations of etching processes for silicon dioxide (SiO_2) with a carbon mask having a 4-nm diameter hole by energetic fluorocarbon ions. The incident ion energy was typically in the range from 200eV to 1000eV. For example, in the case of CF_3+ ion injections, we observed that the depth of the etched out SiO_2 increased with increasing incident ion energy while the channel width became narrower as the etching of SiO_2 went deeper. Tapering of the carbon mask was also observed when the incident ions hit and deform the mask instead of going straight towards the SiO2. Furthermore, if the incident energy was too high (e.g., 1000 eV in this case), closing of the carbon mask hole occurred due to the formation of long carbon chains that moved across the hole and were bonded to the opposite side. Deposition of carbon atoms from the mask onto the sidewalls of the etched SiO_2 was also observed, which caused the formation of silicon carbide and may have impeded horizontal etching of SiO_2.

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[1] **NSTD Postdoc Finalist**

8:40am **PS+AS+EM+SS-MoM2 SF_6/O_2 Plasma Nanotexturing of Silicon: Decoupling How Ion Flux and Ion Energy Matter***, **Guillaume Fischer**[1],* Institut Photovoltaïque d'Ile-de-France (IPVF), France*; E. DRAHI, S.A. FILONOVICH,* Total SA Renewables, France*; E.V. Johnson,* LPICM, CNRS, Ecole polytechnique, Université Paris-Saclay, France

Crystalline silicon (c-Si) solar cell performance can be improved by reducing front surface reflectance. A drastic decrease may be obtained by texturing the surface at the nanoscale ("nanotexturing"), leading to a graded refractive index from air to c-Si. SF_6/O_2 plasma etching of c-Si in a capacitively coupled radiofrequency (CCP-RF) discharge is known to induce spontaneous nanotexturing. This phenomenon – typically resulting in the formation of conical nanostructures (NS) with typical sizes ranging from 30 to 500 nm – occurs through *in-situ* formation of non-volatile inhibitors on the surface. The latter compete with simultaneous physical and chemical etching, and all these mechanisms may be influenced by ion bombardment.

In the present study, the ion energy distribution at the substrate electrode is tuned using Tailored Voltage Waveforms (TVWs) excitation in a reactive ion etching system. TVWs are obtained by adding harmonic frequencies with controlled amplitudes and phase-shifts to the basis driving signal at 13.56 MHz. This technique may give rise to amplitude and slope asymmetries in electronegative plasmas such as the SF_6/O_2 mixture.

Taking advantage of the edge-high total ion flux radial profile on the electrode but with a uniform energy distribution profile, we investigate the influence of both ion energy and ion flux on the nanotexturing process. Process conditions (etching time and driving voltage, i.e. sinusoidal signal or TVWs) are varied, and four samples are simultaneously textured for each set of conditions. The variations in etch rate suggest an ion energy-dependent etching yield. A phenomenological model (etching yield varying with the square root of the ion energy above a threshold at 13 eV) is proposed, and leads to the determination of a clear dependence between the energy weighted ion fluence and the final total hemispherical reflectance of the samples.

This trend is of great relevance for photovoltaic applications, and is explained by the constant increase in NS height during the process, which gradually smoothens the transition of refractive index from air to c-Si. However, the instantaneous ion flux is still observed to influence the aspect ratio (ratio between average height and width of the NS): the higher the ion flux, the higher the aspect ratio. This effect may stem from reduced lateral expansion of inhibitor species on the NS flanks due to the higher ion flux, and will affect the subsequent surface passivation required for photovoltaic applications. Finally, design rules for silicon nanotexturing using SF_6/O_2 plasma are drawn from the observed trends.

9:00am **PS+AS+EM+SS-MoM3 Corrosion Resistance to F and Cl plasma of Yttrium Oxyfluoride (YOF) formed by Sintering***, **Akinobu Teramoto**, Y. Shiba, T. Goto,* Tohoku University, Japan*; Y. Kishi,* Nippon Yttrium Co., Ltd, Japan*; S. Sugawa,* Tohoku University, Japan

Corrosion resistance to the reactive species in some kinds of plasma is very important to construct the reliable semiconductor process equipment. Especially the Fluorine and/or Chlorine plasma have the strong corrosiveness, and then it is strongly required that the inner wall material of the plasma chamber and the components in the plasma chamber have corrosion resistance to them. We have reported the Yttrium oxyfluoride (YOF, Y:O:F=1:1:1) film has the higher resistance to some plasma conditions (N_2/Ar, H_2/Ar, NH_3/Ar, NF_3/Ar, O_2/Ar) than the Y_2O_3 and YF_3 films [1, 2]. In this presentation, we report the corrosion resistance to NF_3/Ar, Cl_2/Ar and O_2/Ar plasma of YOF formed by sintering. The Y, O and F composition was controlled by mixing ratio of the YOF, YF_3, and $Y_5O_4F_7$ before the sintering, as the results, the O concentration was varied from 3 to 12 %. All YOF formed by the sintering are more stable to NF_3/Ar and O_2/Ar plasma than the YOF film and both Y_2O_3 film and formed by sintering. Cl_2/Ar plasma shows the stronger corrosion effect to the Y_2O_3 and YOF's, however the corrosion resistance to Cl plasma of YOF's is higher than the Y_2O_3.

These results indicate that the YOF is much stable against the corrosion by the plasma, and YOF formed by sintering is the promising material to construct the components in the plasma chamber.

Acknowledgement

The plasma irradiation and inspection were carried out in Fluctuation-Free-Facility in Tohoku University.

References

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2. Y. Shiba, A. Teramoto, T. Goto and Y. Kishi, p. 111, AVS 64th International Symp., Tampa, 2017.

9:20am **PS+AS+EM+SS-MoM4 Decay of Hydrogen in NF_3/Ar and O_2/Ar Cleaning Process by Optical Emission Spectroscopy***, **Hanyang Li**, Y. Zhou, V.M. Donnelly,* University of Houston*; J. Chiu, X. Chen,* MKS

Fluorine atom-generating plasmas are commonly used in many cleaning processes after chambers have been exposed to a variety of etching and deposition reactants and products. The most common feed gas used in these applications is NF_3, due mainly to its ease of dissociation. Repeated processing and chamber cleaning cycles can cause changes in the plasma source, thought to be due mainly to an altering of the nature of the chamber wall protective coatings. In the present study, high power density (5 – 50 W/cm^3), low frequency (400 kHz) toroidal inductive plasmas were operated with H_2/Ar (4/96) and N_2/H_2/Ar (3/9/88) feed gases for various periods, alternating with exposure to NF_3/Ar, O_2/Ar, or pure Ar "chamber cleaning" plasmas. H Balmer-alpha optical emission intensity, ratioed to emission from Ar at 750.4 nm, was measured during H_2/Ar exposure and the following cleaning plasma. Hydrogen was detected evolving from the anodized Al plasma source wall coating. The decay of intensity ratio of H/Ar increased with increasing H_2/Ar plasma exposure. NF_3/Ar plasmas enhanced evolution of H, tentatively ascribed to diffusion of F into anodized Al (most likely as F^-), which reacts with H that would otherwise remain trapped in the layer. The HF product then out-diffuses, leading to plasma dissociation and H emission. Conversely, O_2/Ar plasmas suppressed the evolution of H, presumably because O bonds to Al in anodized Al and ties up hydrogen as bound OH.

9:40am **PS+AS+EM+SS-MoM5 Plasma-surface Interactions in the Strongly Coupled Regime***, **Thomas Morgan**,* DIFFER, Netherlands **INVITED**

At high fluxes and densities the interaction of a plasma with the walls of its confinement enter the strongly coupled regime [1], where the mean free paths for collisional processes become much smaller than those of the plasma scale size. The surface morphology in such cases may be pushed far out of equilibrium and in turn the recycling and erosion strongly perturbs the near-surface plasma. Such conditions are reached in high flux plasma processing as well as the exhaust region of future large-scale fusion reactors such as ITER and DEMO. The linear plasma generator Magnum-PSI [2] is uniquely capable of achieving high density low temperature plasmas with high similarity to fusion reactor exhaust fluxes. Using this device the power handling, long term erosion and evolution of plasma facing materials for ITER and DEMO can be studied, as well as the self-organisation effects and novel structures which occur under such conditions. At plasma-liquid metal interfaces considered as advanced wall components this strong coupling can give rise to vapour shielding of the surface, indicating a novel method to limit heat loading damage to wall surfaces in the reactor exhaust [3]. An overview of results will be given showing how this device is addressing urgent questions for ITER, helping to develop advanced walls for DEMO and beyond, and exploiting non-equilibrium for plasma processing.

[1] A.W. Kleyn et al. Phys. Chem. Chem. Phys. 8 (2006) 1761–1774

[2] G. De Temmerman et al. Fusion Eng. Des. 88 (2013) 483-487

[3] G.G. van Eden et al. Phys. Rev. Lett. 116 (2016) 135002

10:40am **PS+AS+EM+SS-MoM8 Tailoring the Surface Properties of Porous Zeolite Constructs using Plasma Processing***, **Angela Hanna**[2], E.R. Fisher,* Colorado State University

Zeolites have been widely used for adsorption, catalysis, and gas separation processes. Despite their extensive use, the ability to control the surface properties of zeolites remains unoptimized. Plasma modification presents an ideal modification methodology with a wide parameter range and the potential to create tailored surface properties and functionalities. Thus, we sought to improve material performance through plasma surface modification, as well as through fabrication of various zeolite constructs (i.e., native zeolites, pellets and electrospun fibers). Moreover, our approach to understand the fundamental plasma chemistry allows us to provide significant insight into mechanisms that will ultimately provide a more thorough evaluation of plasma processing for zeolite surface modification. We employed a range of characterization tools to assess materials before and after plasma treatment and optical spectroscopies to examine the gas-phase of the plasma, both with and without zeolites to evaluate the impact of the material on the gas-phase. X-ray photoelectron

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[1] **Coburn & Winters Student Award Finalist**

[2] **National Student Award Finalist**

spectroscopy (XPS), scanning electron microscopy, and powder X-ray diffraction were utilized to assess surface chemistry, substrate morphology, and bulk characteristics of the material, respectively, before and after plasma exposure. Water contact goniometry was employed to evaluate the surface wettability, where untreated zeolites were nominally hydrophilic. Here, we explored two fluorocarbon (FC) precursors (i.e., C_2F_6 and C_3F_8) to create more hydrophobic surfaces than the untreated materials. XPS analysis reveals surface fluorination and/or formation of a FC coating on the material. $H_2O_{(v)}$ plasmas were also employed to create a more hydrophilic zeolite surface, while maintaining a porous, interconnected network. By also studying the gas-phase, we can glean how the material changes the plasma environment. Species interactions and plasma energetics are intertwined; thus, temporally-resolved data are necessary to accurately probe the intricate dynamics within plasmas. We have investigated formation and destruction mechanisms of key excited state species (i.e., CF, CF_2, OH) to provide mechanistic insight that could be correlated with system energetics data and material properties. Emission spectroscopy was also used to measure the relative gas phase densities of the aforementioned key species as a function of plasma operating parameters (i.e., power, gas mixture, substrate architecture). Our studies have revealed correlations between gas-phase spectroscopic analyses, the gas-surface interface, and the resulting plasma modified surface properties, ultimately leading to improved plasma processes.

11:00am **PS+AS+EM+SS-MoM9 Generation Kinetics of Plasma-induced Electronic Defects in Semiconductor Materials***, **Shota Nunomura**, I. Sakata, K. Matsubara,* National Institute of Advanced Industrial Science and Technology (AIST), Japan

In state-of-the art semiconductor devices, electronic defects strongly influence the device performance. The electronic defects are often generated during the device fabrication, where a variety of plasma processing technology is used for film deposition, gate etching, dopant implantation and so on. Most defects are recovered by post-annealing, however some defects remain in the devices. Because these defects usually deteriorate the device performance, reduction of these defects is required. However, the kinetics of generation and annihilation of the defects are not fully understood yet.

We studied the kinetics of electronic defects in hydrogenated amorphous silicon (a-Si:H) during H_2 and Ar plasma treatments. The generation and annihilation of defects are monitored via in-situ photocurrent measurement during the treatment [1-2]. A decrease in the photocurrent indicates the generation of defects whereas an increase in the photocurrent indicates the annihilation of defects. This photocurrent-based monitoring is highly sensitive in the detection of small amount of defect density (~10^{16}cm^{-3}).

The photocurrents in a-Si:H films under various conditions of H_2 and Ar plasma were measured. From the measurements, we find the following [3]. (i) Each plasma treatment immediately causes the generation of defects, indicated by a strong reduction in the photocurrent. (ii) The defects are generated dominantly by the radicals such as hydrogen atoms (H) and argon metastable atoms (Ar^*). (iii) The residual defects are created by the bombardment of Ar^+ ions rather than H_3^+ ions, radicals and photons. However, the residual defects are recovered mostly by an additional H_2 plasma and post-annealing treatment. (iv) The radicals and photons also generates defects, however these defects are annihilated by the simple post-annealing. The details of the experimental setup, results and discussion are given in the presentation.

This work was supported by JSPS KAKENHI (Grant Number 18K03603 and 15K04717) and NEDO.

[1] S. Nunomura, I. Sakata, and M. Kondo,*Appl. Phys. Express* **6**, 126201 (2013). [2] S. Nunomura and I. Sakata, *AIP Advances* **4**, 097110 (2014). [3] S. Nunomura et al., submitted.

11:20am **PS+AS+EM+SS-MoM10 Evolution of Photoresist Layer Structure and Surface Morphology under Fluorocarbon-Based Plasma Exposure***, **Adam Pranda**, S.A. Gutierrez Razo, J.T. Fourkas, G.S. Oehrlein,* University of Maryland, College Park

Fluorocarbon-based plasma chemistry is an integral component in enabling the pattern transfer step in the semiconductor manufacturing process. Although significant work has gone towards understand the overall etching behavior, surface roughness, and chemistry development for continuous-wave (CW) plasmas with Ar/fluorocarbon admixtures,[1] a complete understanding of the photoresist layer structure evolution and surface roughness distribution has not been well established. Specifically, under high-energy ion bombardment, a dense amorphous carbon (DAC) layer forms at the surface, impacting the etch resistance and surface roughness. For discrete evaluation of the DAC layer/fluorocarbon interaction, we employed a pulsed plasma setup in which a biased, steady-state Ar plasma was used to develop DAC layers of various thicknesses at the photoresist surface, after which fluorocarbon (C_4F_8) pulses of various lengths were introduced. We sought to answer three key questions: 1. How does the fluorocarbon interaction with the DAC layer impact the layer structure? 2. How is the surface roughness affected by the fluorocarbon interaction? 3. How does the pulsed process compare to a CW Ar/C_4F_8 admixture process?

For sample characterization, we utilized a combination of real-time, *in situ* ellipsometry and X-ray photoelectron spectroscopy at various points during the plasma exposure on an industry-standard 193 nm photoresist, several model polymers, and a 3-color-lithography-compatible photoresist that we are developing. Atomic force microscopy (AFM) was used to monitor the surface roughness evolution and the distribution was calculated using a power spectral density (PSD) analysis.

From the combined analyses, we find that the fluorocarbon depletes the DAC layer by a partial conversion of the surface of the DAC layer into an F-rich mixed layer. Furthermore, the mixing of the fluorocarbon into the DAC layer results in an overall smoothening of the sample surface. By comparing the pulsed process to the CW process, we evaluate the significance of the layer structure in determining the surface behavior in response to variations in fundamental plasma parameters such as the ion energy or exposure time.

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).

[1] S. Engelmann et al., J. Vac. Sci. Technol. B Microelectron. Nanom. Struct. **27**, 1165 (2009).

11:40am **PS+AS+EM+SS-MoM11 Fundamental Studies of Plasma Species with Organic Materials of Varying Hydrogen and Oxygen Composition by Computational and Experimental Approaches***, **Yusuke Fukunaga**,* Nagoya University, Japan*; P.L.G. Ventzek, B. Lane,* Tokyo Electron America, Inc.*; A. Ranjan,* TEL Technology Center America, LLC*; M. Sekine, T. Tsutsumi, H. Kondo, K. Ishikawa,* Plasma Nanotechnology Research Center, Japan*; R. Upadhyay,* Esgee Technologies*; L. L. Raja,* The University of Texas at Austin*; G. Hartmann,* McKetta Department of Chemical Engineering, The University of Texas at Austin*; G. S. Hwang,* The University of Texas at Austin*; M. Hori,* Institute of innovation for future society, Japan

Organic film etching is important for semiconductor device fabrication especially as it relates to self-aligned-multiple-patterning in which sub-nanometer scale pattern replication is critical. Even though the etching of organic materials has been studied for decades (e.g., O_2 plasma ashing), new process applications (e.g. ALE) and new chemistry regimes render older models of organic etching such as those employing the Ohnishi parameter of limited use.[1] Existing kinetic models rely on untested assumptions such as the role of dangling bonds as reaction initiating sites.[2] A need exists to revisit the fundamentals of plasma surface interactions as they pertain to the etching of organic films. Moreover, a need exists to incorporate fundamental kinetic models with macroscale models which could be used for process development.

Progress has been slow because of the computational weight of modeling the chemical kinetics and difficulty defining a tractable problem. In this presentation, we describe the use of an integrated modeling framework involving fundamentals-based ab-initio and plasma chemistry simulations with high performance computing to describe chemical kinetics on model polymer systems. In O_2 and Ar plasmas, we use finite carbon size strands with varying degrees of O, OH or H termination as model structures. For simplicity, the structures are polyethylene-like. We use density functional theory (DFT) to model the interactions between plasma species and representative structures. To estimate the relative importance of plasma species and their energy, we derive species and energy flux from a macroscale plasma chemistry model. Both DFT and ab-initio molecular dynamics (AIMD) simulations are used to probe the chemical stability of representative structures to different plasma species (e.g., Ar, O) and energy fluxes. We found that O addition to H terminated structures results in OH group formation on polyethylene by exothermic reaction. Ar ion bombardment formed carbon strands may also be oxidized. The resultant structures (oxo-carbon) are also stable up to large oxygen to carbon ratios. The stability to Ar ion bombardment will be presented. An essential test of any new mechanism is experimental validation. In addition to the computational results, we will present experimental results ranging from basic etch rate measurements to measurements of plasma processed material chemical composition (e.g., XPS).[3]

References:

[1] H. Gokan, *et al.*, J. Electrochem. Soc.: Solid-state Sci. Technol. **130**, No. 1, 143 (1983).

[2] F. D. Egitto, Pure & Appl. Chem. **62**, No. 9, 1699 (1990).

[3] D. U. B. Aussems, *et al.*, Chem. Sci. **8**, 7160 (2017).

Tribology Focus Topic
Room 201A - Session TR+AS+NS+SS-MoM

Tribology Focus Session

Moderators: Mehmet Z. Baykara, University of California, Merced, Prathima Nalam, University at Buffalo - SUNY

8:20am **TR+AS+NS+SS-MoM1 Structural Superlubricity: History, Breakthroughs, and Challenges*, Mehmet Z. Baykara,*** University of California, Merced **INVITED**

The idea of *structural superlubricity* holds immense potential for the realization of nearly frictionless sliding in mechanical systems, with implications for fields as diverse as environmental conservation and space travel. The basic principle of structural superlubricity involves the proposition that friction should diminish at an interface formed by atomically-flat and molecularly-clean crystalline surfaces with different lattice parameters and/or incommensurate orientation. Despite the rather straightforward character of its basic principle, the realization of structural superlubricity under ambient conditions has been challenging due to the requirement of molecular cleanliness at the interface.

In this talk, we will first briefly review three decades of structural superlubricity research by emphasizing important milestones and breakthroughs. Subsequently, we will present results of nano-manipulation experiments from our lab, which demonstrate the remarkable occurrence of structural superlubricity for gold and platinum nano-islands sliding on graphite under ambient conditions. Complementary to the experiments, results of *ab initio* calculations will be discussed, which (i) reveal that the noble metal–graphite interface is expected to remain largely free from contaminant molecules, leading to structurally superlubric sliding under ambient conditions, and (ii) confirm the experimental observation of larger friction forces for platinum, attributable to higher energy barriers encountered during sliding. The experiments additionally demonstrate that the scaling power between friction force and contact size is independent of the chemical identity of the sliding atoms, but is determined by the geometric qualities of the interface. The talk will conclude with a review of remaining challenges for structural superlubricity, in particular those involving size- and deformation-related limits.

9:00am **TR+AS+NS+SS-MoM3 An Examination of the Nature of Bonding during Indentation and Sliding using MD and in-situ Nanoindentation*, Judith Harrison,*** United States Naval Academy **INVITED**

Adhesion between DLC tips and diamond counterfaces was examined using a nanoindentor coupled to TEM and molecular dynamics (MD). Additional MD simulations of sliding contact between the same tip-substrate materials were also carried out. Strong interactions between the surfaces in vacuum led to gradual nanoscale wear of the DLC. Force-separation curves show an approximate correlation between pull-off force and applied load for various contact points, while pull-in force was fairly constant for all contact points and independent of applied load. MD simulations were designed to replicate experiment as closely as possible and used the AIREBO and the REBO+S potentials. DLC tips with the same general shape (which often deviated from the assumed paraboloidal tip geometry due to wear) were brought into contact with diamond surfaces. MD results demonstrate that pull-off force is correlated with bonds formed during contact, providing an explanation of the trends observed in the TEM data. The effects of contact point and hydrogen-termination on pull-off forces and the nature of bond formation during sliding as a function of speed and hydrogen termination will be presented. The results of similar experiments and MD simulations using Si tips in contact with diamond counterfaces of adhesion and sliding using the ReaxFF potential will also be discussed.

9:40am **TR+AS+NS+SS-MoM5 The Chemistry of Friction, Wear, and Tribofilm Growth on 2D Materials*, Jonathan Felts,*** Texas A&M University **INVITED**

The evolution of a sliding interface between two objects is difficult to theorize, predict, and measure due to the complexity of the interface, which is often described phenomenologically. Here we utilized a nanometer sized single asperity of an atomic force microscope tip sliding against atomically flat graphene and graphene oxide to study the origins of friction, wear, and tribofilm growth phenomena at the atomic scale. We hypothesize that all of the observed contact phenomena at the macroscale can be described using fundamental thermochemistry. At low applied tip loads, the friction of graphene oxide is non-monotonic with tip velocity, initially increasing for speeds from 100 – 10,000 nm/s, followed by a decrease and a subsequent increase above 50,000 nm/s. At sufficiently high applied loads, we observe wear of oxygen groups from graphene oxide at temperatures between 50-400 °C and loads between 10-700 nN, and find an exponential increase in wear rate with applied load. For the case of an electrically biased tip oxidizing pristine graphene, the oxidation rate somewhat paradoxically increases with applied load, despite previously observed enhancement in wear rate with load. All of the above observations can be understood in the context of mechanically driven thermochemical reactions. The friction behavior depends on two competing factors—aging of the sliding contact due to chemical bonding between tip and substrate, and hopping of unbonded tip atoms between graphene lattice sites. Atomic wear of graphene oxide is well described by the tilted potential energy surface theory of mechanically driven chemistry, which predicts a non-linear reduction in the energy barrier with applied load. We further show that the tilted potential energy surface model also well describes the enhancement of oxidation rate. The work presented here creates a foundation for describing the mechanics of sliding contacts as chemical processes, and further paves the way towards quantitatively understanding how mechanical force drives chemical reactions in general.

10:40am **TR+AS+NS+SS-MoM8 Nanomechanics of Soft, Hierarchical Polymer- and Biological-Networks*, Prathima Nalam,*** University at Buffalo - SUNY **INVITED**

Soft networks based on synthetic polymer chains or biological filaments, with architecture that are anisotropic or hierarchical in nature, offer a path towards the development of tough and reliable flexible structures. These structures find applications in numerous areas including healthcare delivery, environmental purification systems, energy storage systems, flexible electronics, and tribology. Further, the ability of these networks to present a wide range of tunable functional properties, through alterations in the chemical structure of the monomers, synthesis or operational conditions, etc., which otherwise is rarely possible with other hard materials, promise the development of smart materials. In this study, we present the nanomechanical and nanotribological behavior of two stimuli-responsive networks consisting of (a) polyelectrolyte films with a thin layer of chitosan (CH) grafted on top of poly (acrylic acid) (PAA) brushes (CH/PAA) and (b) naturally grown mycelium-based networks. The CH/PAA network is a synthetic hierarchical structure, in which each layer exhibits a strong structural change with variation in solution pH. On the other hand, Mycelium is a soft biological network (derived from mushrooms) composed of multicellular or unicellular filaments, known as hyphae, with anisotropic micro-architecture.

A detailed investigation of the depth-dependent elastic moduli on these networks is conducted using atomic force microscope (AFM, Oxford Instruments) to study the impact of local structural heterogeneity of the network on its mechanical properties. A colloid-attached AFM cantilever was employed to study the surface interactions and to indent the material in the linear elastic deformation regime. The study of the impact of the network structure on the material rigidity, measured at both nano- and macro- scales, has enabled to probe the validity of affine network deformation theories for hierarchical networks. With this understanding, the design and development of antibacterial platforms (with CH/PAA platforms) and water-filtration membranes (with mycelium networks) using hierarchical soft structures is discussed.

11:20am **TR+AS+NS+SS-MoM10 Mechanisms for Controlling Friction and New Approaches for Achieving Superlubricity Regime in 2D Materials*, Diana Berman,*** University of North Texas*; A. Erdemir, A.V. Sumant,* Argonne National Laboratory **INVITED**

Friction is an important aspect of many areas of everyday life. Varieties in mechanical systems from nano to macroscale and efforts to minimize energy losses intersect with challenges of controlling the friction. The popularity of recently discovered 2D materials and their usefulness for multiple applications enabled understanding the friction at a more fundamental level and opened new routes for manipulating friction to superlubricity or near zero friction values.

Here, we review the basic mechanisms that complies the frictional energy dissipation, such as wear, molecular deformation, thermal effect, electronic effect, bonding, environment and chemistry, phonons, and structural effect. We present the case studies highlighting how these mechanisms are controlled in 2D materials. Finally, we highlight recent advances in implementing 2D materials for friction reduction to superlubricity across scales from nano- up to macroscale contacts. We show that nanoscale superlubricity mechanisms originating from the formation of frictionless nanoscale systems, as in case of graphene-nanodiamond scrolls and carbon nanoonion structures, can be successfully transferred to macroscale effects. Development of 2D materials opened a new pathway for manipulating friction, which makes superlubric friction today's reality.

References:

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[2] D. Berman, et al., special issue in Diamond and Related Materials, 54, 91 (2015).

[3] D. Berman, et al., Materials Today 17 (2014) 31-42.

[4] D. Berman, et al., Science, 348 (2015) 1118-1122

Applied Surface Science Division
Room 204 - Session AS-MoA

Multitechnique Applications-When More techniques are Better than One

Moderator: Karen Gaskell, University of Maryland, College Park

1:20pm **AS-MoA1 Overcoming Obstacles in Surface and Interface Characterization of All Solid-State Lithium Battery Materials*, Natalie Seitzman,*** Colorado School of Mines*; H. Guthrey, D. Sulas, S. Johnston,* National Renewable Energy Laboratory*; J. Nelson Weker,* SLAC National Accelerator Laboratory*; H. Platt,* Solid Power, Inc.*; M. Al-Jassim,* National Renewable Energy Laboratory*; S. Pylypenko,* Colorado School of Mines

Novel battery technologies are a key route to sustainable energy, but new chemistries come with new failure mechanisms that present characterization challenges. The nature of many promising next-generation batteries makes them inherently difficult to study, and multiple techniques must be combined to capture the relevant phenomena. For all-solid-state lithium batteries, one challenge is the reactivity of the battery components restrict which types of techniques may be used. Additionally, although the interfaces are of great interest, processes that expose them for characterization have unknown, likely deleterious effects on their integrity. Therefore, in order to understand characterization of surfaces and interfaces in batteries, bulk characterization and in situ characterization at multiple scales is also needed.

The focus of this work is probing the morphological evolution, including dendrite formation, of the electrode-electrolyte interface between lithium metal and β-Li_3PS_4 solid electrolyte. This is done through a combination of lock-in thermography, x-ray tomography, in situ scanning electron microscopy (SEM), and x-ray absorption near edge structure (XANES). We used thermography as a first step to identify trends in location of dendritic features, to guide techniques with smaller fields of view and greater resolution, such as SEM. X-ray tomography enables characterization of the interfaces without deconstructing the device or exposing the interfaces needed for surface characterization. Therefore, micro-tomography was performed both to study morphological changes and to check that results observed in other experiments with modified samples—such as nano-tomography, which required a focused ion beam to cut and lift out micron-scale samples—are consistent with the behavior of unaltered materials. In situ SEM cycling experiments and windowless energy dispersive spectroscopy (EDS) provided morphological and chemical characterization of the changing surfaces and interfaces with high spatial resolution. Detailed chemical characterization of the bulk material was obtained with XANES at the sulfur and phosphorus K-edges. This work furthers the development of surface and interface characterization of battery materials and moves toward localized, nanoscale characterization.

1:40pm **AS-MoA2 *In-situ* Complementary XPS and Raman Analysis of Technologically Important Materials*, Paul Mack,*** Thermo Fisher Scientific, UK

In this work, X-ray Photoelectron Spectroscopy (XPS) and Raman spectroscopy have been used to analyse technologically relevant materials. An XPS spectrometer (Thermo Scientific Nexsa) was configured with a Raman spectrometer, enabling *in-situ* complementary analysis. XPS is a surface sensitive technique, with an information depth between 0-10nm. It is chemically selective, allowing the use to investigate different bonding states of the same element. Raman is a vibrational spectroscopy, which is more bulk sensitive (typically on the µm scale). It can also give some information about chemistry, but it also yields complementary structural or bonding information.

The battery-relevant material, lithium cobaltite ($LiCoO_2$) was analysed in the Nexsa spectrometer. $LiCoO_2$ is used in the cathode of some lithium-ion batteries. During charge/discharge cycling the cathode may degrade, causing the creation of the mixed oxide, Co_3O_4. XPS and Raman data were acquired from two different points on a $LiCoO_2$ cathode. Differences in cobalt and lithium bonding states at the surfaces of the two different points were analysed with XPS, before and after argon ion cleaning. Complementary Raman analyses were performed at the same points in the same instrument. The Raman data allowed identification of the bulk material, together with an evaluation of cobalt oxide degradation products.

The second sample analysed in this work was a boron nitride film deposited onto a copper substrate. The goal of the deposition was to create an atomically thin hexagonal boron nitride structure (h-BN), analogous to graphene. It was found that the deposition created an inhomogeneous distribution of boron nitride, which was optically invisible. XPS mapping and imaging (Thermo Scientific SnapMap) was used to locate the boron nitride on the copper substrate. The XPS image was used to define the analysis points for further XPS and Raman analysis. XPS allowed the chemical bonding states of the boron and nitrogen to be identified, together with an identification of contaminants on the surface. The structure of the boron nitride, such an sp^2 and sp^3 configurations, was evaluated with Raman spectroscopy.

2:00pm **AS-MoA3 Integration of Laboratory Experiments. Spectroscopy, and Microscopy to Investigate the Reactivity of Metals in Mine Wastes*, José Cerrato,*** University of New Mexico **INVITED**

The reaction mechanisms affecting metal transport in mine waste sites was investigated by integrating laboratory experiments, microscopy, and spectroscopy. Metal release from these mine wastes could pose potential health risks for neighboring communities. Spectroscopy analyses on the first site located in Northeastern AZ (Navajo tribe) suggest that U-V phases are present in abandoned mine wastes; the dissolution of these U-V phases is relevant to U and V transport. Electron microprobe and electron microscopy analyses on the second site located in Laguna, NM (Pueblo tribe) suggest that U-Si and U-P phases on mine wastes from which could be a source for U in neighboring surface waters. The presence of U(VI) and U(IV) was detected with X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS). The presence of coffinite encapsulated in particulate organic matter was identified in mine waste samples using X-ray diffraction (XRD) and transmission electron microscopy (TEM). Accumulation of U in roots of plants from these mine waste sites was also investigated.

3:00pm **AS-MoA6 Surface Phase, Morphology, and Charge Distribution Transitions on Vacuum and Ambient Annealed Perovskites: A Case Study on $SrTiO_3$(100)*, Omur Dagdeviren*[1]**, *G. Simon, K. Zou, C. Ahn, F.J. Walker, E.I. Altman, U.D. Schwarz,* Yale University

The surface structures of $SrTiO_3$(100) single crystals were examined as a function of annealing time and temperature in either oxygen atmosphere or ultrahigh vacuum (UHV) using noncontact atomic force microscopy (NC-AFM), Auger electron spectroscopy (AES), and low-energy electron diffraction (LEED) [1]. Samples were subsequently analyzed for the effect the modulation of their charge distribution had on their surface potential. It was found that the evolution of the $SrTiO_3$surface roughness, stoichiometry, and reconstruction depends on the preparation scheme. LEED revealed phase transitions from a (1×1) termination to an intermediate $c(4\times2)$ reconstruction to ultimately a $(\sqrt{13} \times \sqrt{13})-R33.7°$ surface phase when the surface was annealed in an oxygen flux, while the reverse transition from $(\sqrt{13} \times \sqrt{13})-R33.7°$ to $c(4 \times2)$ was observed when samples were annealed in UHV. When the surface reverted to $c(4\times2)$, AES data indicated decreases in both the surface Ti and O concentrations. These findings were corroborated by NC-AFM imaging, where initially TiO_2-terminated crystals developed half-unit cell high steps following UHV annealing, which is typically attributed to a mix of SrO and TiOSrO and TiO_2terminations. Surface roughness evolved nonmonotonically with UHV annealing temperature, which is explained by electrostatic modulations of the surface potential caused by increasing oxygen depletion. This was further corroborated by experiments in which the apparent roughness tracked in NC-AFM could be correlated with changes in the surface charge distribution that were controlled by applying a bias voltage to the sample. Based on these findings, it is suggested that careful selection of preparation procedures combined with application of an electric field may be used to tune the properties of thin films grown on perovskite substrates.application of an electric field may be used to tune the properties of thin films grown on perovskite substrates.

[1] O. E. Dagdeviren et al., Physical Review B **93**, 195303 (2016)

3:40pm **AS-MoA8 In-situ Characterisation of Graphene using combined XPS and Raman Spectroscopy: Removal of Polymer Residue by Ar Gas Cluster Ion Beams*, Barry Brennan,*** National Physical Laboratory, UK*; P. Mack,* Thermo Fisher Scientific, UK*; A. Centeno, A. Zurutuza,* Graphenea, Spain*; A.J. Pollard,* National Physical Laboratory, UK

The transfer of chemical vapour deposition grown 2D materials to a relevant substrate material typically involves deposition of a thin polymer layer, usually PMMA, as a handle to transport the 2D material, which is then dissolved in solvent. Any polymer residue is then typically further reduced in a thermal annealing step, designed to break down the polymer

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[1] **NSTD Student Award Finalist**

chain and remove it from the surface. However, this is rarely fully effective, with trace PMMA residue usually detected. This can then affect the electrical and physical properties of the 2D layer, and prevent consistency in the final material. Recently, a number of mechanisms have been explored to further improve the quality of the transferred layer, from introducing further solvent and annealing steps, to the use of plasmas, and argon gas cluster ion beams (GCIB), to remove any remaining residue. In this study, we explore in detail the use of size selected argon GCIBs to clean polymer residue from a CVD-grown graphene surface. Due to the distribution of the charge applied to the cluster over the individual argon atoms, the energy per atom can be tuned to <0.5 eV/atom, significantly below the bond strength of the graphene, but sufficiently energetic to remove polymeric material.

In order to characterise this, a combination of techniques are needed to thoroughly confirm the removal of polymer material, as well as show there is no impact to the underlying graphene. Ideally these techniques would be in-situ and confocal in nature in order to prevent modifications to the sample surface after cleaning, as well as provide confidence in the measurements. To this end, in this study we used the Thermo Scientific Nexsa X-Ray Photoelectron Spectrometer (XPS) system which allowed us to carry out correlative XPS, REELS and Raman spectrometry in-situ from the same area of a graphene sample during GCIB cleaning. This meant we could examine changes in the chemical composition of the graphene surface as polymer material was removed, while monitoring changes in the Raman spectra to determine whether any defects were being generated in the graphene during the cleaning process. The changes in the sample were further probed using 3D time of flight secondary ion mass spectrometry (ToF-SIMS) imaging, to clearly show the removal of polymer materials during GCIB cleaning, while leaving the underlying graphene layer intact. Through the combination of these measurements, we are able to determine that by keeping the energy per argon atom less than 1 eV, we can prevent the introduction of defects to the graphene layer, as well as significantly decrease the level of contamination present on the graphene surface.

4:00pm **AS-MoA9 Topography-corrected TOF-SIMS Chemical Imaging of Chip Interconnect Surfaces***, **Conor Thomas**, B. Singh, R. Wang,* IBM Systems Division

Next generation computing systems are driving increasingly complex packaging architectures and interconnection techniques to meet higher performance and bandwidth requirements at smaller feature sizes. First-level packaging techniques that incorporate controlled collapse chip connections (C4) in flip-chip applications have become critical to enable near-future microelectronics packaging. Conventional C4 technology uses solder bumps for off-chip interconnections after back end of line wafer fabrication. Solder-based flip-chip technology is currently the industry standard with a proven track record of performance, reliability, and ease of manufacturing at low-cost. However, increasing I/O requirements are pushing the limits of interconnection pitch scalability below 50µm, resulting in a higher spatial density of solder bumps and reduction in solder volume per bump.

The surface cleanliness of fine-pitch solder bumps before chip attachment plays an important role in the solder wetting and reliability of the chip-package interconnect structure. In both flip-chip mass reflow and thermo-compression bonding techniques, the solder bump surfaces go through several assembly steps before chip join and are exposed to potential sources of contamination. Unfortunately, the solder bump surfaces are challenging to study by traditional surface characterization techniques like x-ray photoelectron spectroscopy, Auger electron spectroscopy, and secondary ion mass spectrometry due to the relatively small size of the bumps, the mixed conducting and insulating environments of the sample, and the high curvature of the bumps, respectively. These challenges have only been exacerbated by the decreasing size of the bumps.

Here we describe a new approach to characterize modern solder bumps using a time-of-flight secondary ion mass spectrometer (TOF-SIMS) with an atomic force microscope (AFM) integrated in the same vacuum chamber. We can correlate high spatial resolution TOF-SIMS images with AFM topography images to generate topography-corrected chemical images. With this method we can chemically and spatially characterize the contaminants on solder bump surfaces. This method will be compared with results from Auger electron spectroscopy, our standard method of characterizing solder bump surfaces. We will discuss the important considerations for TOF-SIMS imaging of these highly curved surfaces and approaches to correlate images taken by TOF-SIMS and AFM.

4:20pm **AS-MoA10 Combining the Benefits of GCIB-ToF-SIMS, MALDI-FTICR-MS and LC-MS/MS for Location specific Lipid Identification in Planarian Flatworm Tissue Sections***, **Tina Angerer**,* University of Washington*; D. Velickovic, C. Nicora, C.R. Anderton,* Pacific Northwest National Laboratory*; D.J. Graham, L.J. Gamble,* University of Washington

Phagocata gracilis are planarian, non-parasitic flatworms. Planarians are best known for their fascinating regenerative abilities, requiring a complex interplay of a wide range of molecules. The regeneration process and the molecules involved are still poorly understood. Most notably there is a lack of lipid and fatty acid data, a diverse group of molecules fulfilling numerous functions such as energy storage and cell signaling.

To gain a better understanding of the lipidomic landscape in planarians we analyzed positive and negative ions from longitudinal sections of *P. gracialis* with MALDI-FTICR-MS and ToF-SIMS along with homogenized whole worm extracts with LC-MS/MS.

Imaging MALDI-FTICR-MS (15T, Bruker Solarix) provides location specific (50 µm/pixel), ultra-high mass resolution (R≈250,000 @m/z=400) and ultra-high accuracy (<1ppm) lipid data capable of distinguishing intact lipid species of similar exact mass and showing their distribution in the tissue. The drawbacks for this technique are that the spatial resolution is too low to clearly identify features within the worm and its low fragmentation rate. While beneficial for molecular peak intensities, the lack of fragments does not allow for specific lipid assignments with structural information (e.g. lipid headgroup and both fatty acid chains identified).

Imaging GCIB-ToF-SIMS (J105, Ionoptika) generates high mass accuracy (< 5ppm), cell/organ-specific data (3 µm/pixel) consisting of intact lipids, lipid fragments and fatty acids. The moderate mass resolution (R≈10,000@m/z=700) is sufficient to resolve most lipid species. Mass peaks consisting of more than one species are indicated by broad and/or asymmetric peaks with poor mass accuracy. However co-localizing fragments can add confidence for the assignment of overlapping species, provide us with structural information and allow for unambiguous identification of resolved peaks.

LC-MS/MS (Thermo Velos Pro Orbitrap) separates different lipid species prior to fragmentation so, in contrast to SIMS, the observed lipid fragments are guaranteed to stem from the analyzed species. The drawback with this technique is that it provides no location specific information. Similar to SIMS, lipids with similar mass are not separated leading to mixed fragments in the MS/MS data. Comparing LC-MS/MS to SIMS data shows that the same lipid fragment species are present in both spectra.

This work demonstrates that only by correlating all 3 techniques can we get highly accurate, high mass, high spatial resolution, structural and location specific lipid information. Together this data provides detailed information about all major structures and organs within planarians.

Biomaterial Interfaces Division
Room 101B - Session BI+AS+IPF+MN-MoA

Advanced Imaging and Structure Determination of Biomaterials Research

Moderators: Dan Graham, University of Washington, Axel Rosenhahn, Ruhr-University Bochum, Germany

1:20pm **BI+AS+IPF+MN-MoA1 NMR Relaxometry as a Medical Diagnostic***, **Michael J. Cima**,* Massachusetts Institute of Technology **INVITED**

This talk will describe the diagnostic capabilities of magnetic resonance imaging (MRI) when brought to the patient bedside. Rather than imaging, NMR can be used for important chemical/physiologic diagnostic endpoints. Two will be discussed here; quantifying fluid overload and measurement of hypoxia within tumors. Assessment of intra- and extra-vascular volume is integral in managing patients with heart, liver, and kidney disease as volume status is closely linked to mortality. Commonly used determinants of volume status, such as physical exam and ultrasonography, lack sensitivity and specificity and require expertise in clinical practice. This talk reports on nuclear magnetic resonance (NMR) methods to a portable and clinically useful device. A clinical study with hemodialysis patients and age-matched healthy controls was performed at MGH. The T2 relaxation times of study participants' legs were quantified at multiple time points with both a 1.5T clinical MRI scanner and a custom 0.27T single-voxel MR sensor. The results showed that first sign of fluid overload is an increase in the relative fraction of extracellular fluid in the muscle. The relaxation time of the extracellular fluid in the muscle eventually increases after more fluid is accumulated. Importantly, these MR findings occur before signs of edema are detectable on physical exam. Solid tumors are often hypoxic and characterized by an extreme lack of oxygen. Tumor hypoxia imparts significant negative outcomes for patients but is highly variable within cancer types and patient populations. Many of these poor clinical outcomes can be tied to hypoxic-induced radiotherapy resistance. Resistance to radiotherapy in hypoxic regions can be overcome by increasing the dose delivered but exposure limitations of healthy tissue and organs must be considered. The lack of a viable quantitative clinical oxygen measurement method prevents safe dose escalation in these patient populations. Here we report on a silicone-based quantitative oxygen sensor. The MRI contrast of this material depends on dissolved oxygen. Thus, the material functions as a first of its kind solid-state contrast agent. The sensor leverages the existing MRI hardware, which is part of the current clinical work flow, to map tumor oxygen content. This information can then be integrated into the dose planning process clinicians currently conduct to selectively and safely boost dose to low oxygen tumor subvolumes. This sensor is approved by the institutional review board at Dana Farber Cancer Center for a clinical trial in patients locally advanced cervical cancer.

2:00pm **BI+AS+IPF+MN-MoA3 Direct Observation of Cell Signaling Proteins Interacting with a Model Cell Membrane by Sum Frequency Generation Vibrational Spectroscopy***, T.W. Golbek,* Oregon State University*; T. Weidner,* Aarhus University, Denmark*; C.P. Johnson, **Joe Baio,*** Oregon State University

Proteins that contain C2 domains are involved in a variety of biological processes including encoding of sound, cell signaling, and cell membrane repair. Of particular importance is the interface activity of the C-terminal C2F domain of otoferlin due to the pathological mutations known to significantly disrupt the protein's lipid membrane interface binding activity, resulting in hearing loss. Therefore, there is a critical need to define the geometry and positions of functionally important sites and structures at the otoferlin-lipid membrane interface. Here we describe the first *in situ* probe of the protein structure of otoferlin's C2F domain interacting with a cell membrane surface. To identify this protein's structure at the lipid interface we applied sum frequency generation (SFG) vibrational spectroscopy and coupled it with simulated SFG spectra to observe and quantify the otoferlin C2F domain interacting with model lipid membranes. A model cell membrane was built with equal amounts of phosphoserine (PS) and phosphocholine (PC). SFG studies that examined the ordering of the lipids that make up the model membrane, demonstrate that lipid fusion occurs after docking of the otoferlin C2F domain via the observation of a 62% increase in amplitude from the SFG signal near 2075 cm^{-1} assigned to specific groups within the model membrane. This increase is related to lipid ordering caused by the docking interaction of the otoferlin C2F domain. SFG spectra taken from the amide I region contain peaks near 1621 cm^{-1} and 1672 cm^{-1} related to the C2F domains beta-sandwich secondary structure, thus, indicating that the domain binds in a specific orientation. By mapping the simulated SFG spectra to the experimentally collect SFG spectra, we found the C2F domain of otoferlin orients 32° normal to the lipid surface. This information allows us to map what portion of the domain directly interacts with the lipid membrane. Furthermore, we show first experimental view of any C2 domain of otoferlin docked at the membrane interface, thereby, validating SFG as a method to probe C2 domain-membrane interfaces.

2:20pm **BI+AS+IPF+MN-MoA4 Vibrational Sum-frequency Scattering Spectroscopy for the Characterization of Protein Fiber Structures and their Surface Interactions in Biological Environments***, **Patrik K. Johansson**, D.G. Castner,* University of Washington

Biological processes are typically regulated by interactions at the interface of 3D structures, such as the membrane of cells or protein fiber surfaces. Collagen (the most common protein in mammals) forms large fibers that are responsible for the structural integrity of tissues. The structure, organization and interactions of these fibers are furthermore important for the survival, communication, migration, and proliferation of cells.

Investigating protein fiber interactions is challenging, particularly under biological conditions where the fibers exist in a 3D aqueous environment. Many techniques cannot interrogate interfaces buried in the bulk of a solvent and therefore require 2D surface models, while others need extensive purification and sample preparation. These approaches may not capture all key characteristics of the fiber surface structure and interactions in the real sample. However, vibrational sum-frequency scattering (SFS) spectroscopy, with inherent contrast for local molecular ordering, can be utilized towards these important goals.

As a first demonstration, we have applied SFS to protein fibers in aqueous environments, self-assembled from collagen type I. We detected signals from the amide I band and the N-H stretching vibrations, both of which are related to the specific protein backbone structure. Signals from the C-H stretching and bending vibrations were also identified, which are more associated with the side-chains in the fibers. The angular scattering patterns for the backbone (amide I) and side-chain (C-H stretches and bends) signals are different, making the spectra dependent on the angle of detection. While the backbone signals are dominant in the phase-matched direction, the side-chain signals remain high also at large scattering angles. Distinctions in the organizational symmetry and the relative fiber surface contribution to the overall signal are hypothesized as reasons for this observation.

Finally, we are investigating the impact of changes to the environment (e.g. ionic strength, pH, surfactants) on the shape of spectra and scattering patterns for the detected SFS signals. This could yield new insights to the structure and dynamics of collagen fibers in biological settings. The relevance of such investigations is enhanced by the fact that detection of vibrations from the surrounding molecules is a direct observation of their interactions with the collagen fiber surface, which thus can be correlated with the fiber structure. The relative orientations for the detected groups can also be obtained via vibrational SFS polarization analysis, for a deeper understanding of biomolecular interactions in biological processes.

2:40pm **BI+AS+IPF+MN-MoA5 How Proteins Grow Calcium Carbonates – The Mechanism of Vaterite Bioprecipitation Studied at the Molecular Level by Sum Frequency Generation Spectroscopy***, H. Lu,* Max Planck Institute for Polymer Research, Germany*; S. Roeters,* Aarhus University, Denmark*; H. Lutz, M. Hood, A. Schäfer,* Max Planck Institute for Polymer Research, Germany*; R. Muñoz-Espí,* Universidad de Valencia, Spain*; M. Bonn,* Max Planck Institute for Polymer Research, Germany*; **Tobias Weidner**,* Aarhus University, Denmark

Proteins can act as Nature's engineers at interfaces and manipulate hard tissue growths. Specialized peptides can bind and release specific mineral facets and grow the intricate mineral morphologies found in diatom cell walls, mollusk nacre, but also human teeth and bone. Taking clues from Nature we aim at understanding the mineralization processes at the molecular level and to develop design rules for biogenic nanophase materials. Mineral proteins control the biogenesis of $CaCO_3$ by selectively triggering the growth of calcite, aragonite or vaterite phases. The templating of $CaCO_3$ by proteins must occur predominantly at the protein/$CaCO_3$ interface. Surprisingly, molecular-level insights into the interface during active mineralization have been lacking. Here, we investigate the role of peptide folding and structural flexibility on the mineralization of $CaCO_3$. We discuss the mineral activity of amphiphilic peptides based on glutamic acid and leucine with *ß*-sheet and *α*-helical secondary structures. While both sequences lead to vaterite structures, the *ß*sheets yield free-standing vaterite nanosheet with superior stability and purity. Surface-specific spectroscopy studies and molecular dynamics simulations reveal that the interaction of calcium ions with the peptide monolayer restructures both the peptide backbone and side chains. This restructuring enables effective templating of vaterite by mimicry of the vaterite (001) crystal plane. The approach is universally applicable to mineral peptide engineering. We will discuss how analogous peptide designs can be used to steer the growth not only of calcium carbonates but also calcium oxalates.

3:00pm **BI+AS+IPF+MN-MoA6 ToF-SIMS Imaging of Chemical Modifications in Topographically Challenging Materials***, **Michael Taylor**, D.J. Graham, L.J. Gamble,* University of Washington

Three-dimensional (3D) porous materials are applied in a variety of areas within materials science[1]. Pores in catalysts provide a high surface reaction area, pores in biofilters facilitate fluid movement for biomolecule capture, and pores in tissue engineered constructs allow for cellular ingress and vascularization. These applications require surface modifications to add specific functionality to their surfaces. The successful functionality of these materials is related to the ability of these modifications to reach all surfaces of the pores. However, it is challenging to characterize these complicated materials and verify the presence and distribution of these surface modifications. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is a powerful label-free surface analysis tool that can be used to image the molecular composition of cells, tissues and polymers. Porous 3D materials however, are non-ideal for ToF-SIMS analysis as the technique is highly surface-sensitive, topography on the order of microns can inhibit the ability to produce secondary ions related to surface modifications. To solve this problem we have developed a methodology for filling voids in porous materials to produce a surface where ToF-SIMS imaging may be performed. A embedding process for porous materials with poly(vinyl alcohol)(PVA) is detailed followed by freezing and cryo-sectioning to expose the modified scaffold interior. Here, we demonstrate the versatility of this method by high spatial resolution 3D imaging of a number of surface modifications in PCL poly(caprolactone) scaffolds^2. Characterisation of fluorocarbon (FC) films deposited using octofluoropropane (C3F8) plasma enhanced chemical vapor deposition (PECVD) will be demonstrated, showing that increased treatment times deposits uniform coatings while shorter treatment results in a gradient distribution of FC throughout the PCL scaffold. Additionally we show data on imaging immobilized/adsorbed proteins within PCL scaffolds. Using this methodology we demonstrate that high spatial resolution label-free 3D imaging of chemical modifications in materials with complex geometries is now possible with ToF-SIMS.

Refs:

(1) Yang, X.-Y.; Chen, L.-H.; Li, Y.; Rooke, J. C.; Sanchez, C.; Su, B.-L. Hierarchically Porous Materials: Synthesis Strategies and Structure Design. *Chem. Soc. Rev.***2017**, *46* (2), 481–558 DOI: 10.1039/C6CS00829A.

(2) Taylor, M. J.; Aitchison, H.; Hawker, M. J.; Mann, M. N.; Fisher, E. R.; Graham, D. J.; Gamble, L. J. Time of Flight Secondary Ion Mass Spectrometry—A Method to Evaluate Plasma-Modified Three-Dimensional Scaffold Chemistry. *Biointerphases***2018**, *13* (3), 03B415 DOI: 10.1116/1.5023005.

3:40pm **BI+AS+IPF+MN-MoA8 Imaging Plant and Plant Growth-Promoting Bacteria Interactions Using Time-of-Flight Secondary Ion Mass Spectrometry***, **Xiao-Ying Yu**, R. Komorek, Z.H. Zhu, C.J. Jansson,* Pacific Northwest National Laboratory

We present the first imaging and spectra results of plant root interactions with plant growth-promoting bacteria (PGPB) using time-of-flight secondary ion mass spectrometry (ToF-SIMS), showing the successful application of delayed image extraction to study plant biology. Compared to MALDI (Matrix Assisted Laser Desorption Ionization), an imaging mass spectrometry technique widely used in plant studies,[1] SIMS is less destructive and provides submicrometer spatial mapping of molecular species of importance in metabolic processes. *Brachypodium distachyon* (Brachypodium), a genomics model for bioenergy and native grasses, is used due to its small diploid genome, close phylogenetic links to other grass species, relative ease of genetic transformation, short life cycle, small stature, and simple growth requirements.[2] Plant growth-promoting bacteria (PGPB) such as *Pseudomonas* and *Arthrobacter* were introduced to Brachypodium roots prior to analysis, and their potential effect on root extrusion was studied using ToF-SIMS imaging. Specifically, delayed image extraction was used in data acquisition. This approach was chosen to obtain high mass and high spatial resolutions.[3] Excellent SIMS imaging gives topographical description of the root surface with and without PGPB interactions. Distinctive characteristic peaks are observed, indicating compositional changes with and without PGPB introduction to the root surface beside visible surface morphological variations. Our initial results demonstrate that ToF-SIMS is a promising imaging mass spectrometry tool to study plant biology and root-microbe interactions and provide molecular-level insight at the biointerface with high spatial resolution.

References:

[1] D Sturtevant *et al.*, Three-dimensional visualization of membrane phospholipid distributions in Arabidopsis thaliana seeds: A spatial perspective of molecular heterogeneity, Biochimica et Biophysica Acta (2017),**1862**(2)*,* 268-81.

[2] T Girin *et al.*, Brachypodium: a promising hub between model species and cereals, J. Experimental Botany (2014),**65**(19)*,* 5683-96*.*

[3] QP Vanbellingen *et al.*, Time-of-flight secondary ion mass spectrometry imaging of biological samples with delayed extraction for high mass and high spatial resolutions, Rapid Comm. Mass Spectrom. (2015), **29** (13), 1187-95.

4:00pm **BI+AS+IPF+MN-MoA9 Imaging of Cells and Tissues with Helium Ion Microscopy***, J.A. Notte, D. Wei, **Chuong Huynh**,* Carl Zeiss Microscopy, LLC

Both optical and electron microscopy are well established techniques in the life sciences with established protocols for imaging and sample preparation. However the newly developed helium ion microscope has some unique advantages, and is gaining a reputation for providing insightful, easy to interpret images over a wide range of biological samples and bio-materials. This presentation serves as both an introduction to this novel technique and a review of recent results.

Because helium ions do not suffer appreciably from diffraction effects, they can be focused to a sub-nanometer probe, providing nanometer scale image resolution with a depth of focus that is well suited to complex surfaces and structures. As helium ions interact with the sample, they provide an abundance of secondary electrons that convey surface-specific and topographical information. Distinctly different from the conventional (gallium) focused ion beams, helium ions do not significantly damage the sample from the sputtering process. And importantly, helium ion microscopy is not affected by charging artifacts when imaging insulating materials, even glass slides, so there is no need for metal over-coating which would otherwise obscure finer details.

Example images will include a pancreatic cell membrane showing the pores and cilia present on their natural surfaces. Other examples will show the complex structure of the principal cell and intercalated cells of the collecting duct of a rat kidney. Other imaging results from diverse fields include stony corals, collagen networks, bone minerals, stereocilia, otoconia, actin filaments, and cryptococcus neoformans. False colorized images of the multi-ciliated epithelial trachea of an adult mouse and T4-phages will also be presented. Finally, new results will be shown from the SIMS spectrometer which provides elemental and isotopic information, and can be the basis for true colorizaton.

In this talk, an emphasis will be placed on the physics principles that enable these imaging results. The selected examples serve to demonstrate the breadth of results that can be attained with this relatively new technique.

4:20pm **BI+AS+IPF+MN-MoA10 Quantitative Analysis of Electrolytes in Microliter-size Blood Drops Congealed via HemaDrop™ using Ion Beam Analysis and SIMNRA***, H. Thinakaran, S.R. Narayan, J.M. Day, **Nicole Herbots**, F.J. Ark, B. Wilkens, M. Mangus, R.J. Culbertson,* Arizona State University

Accurate analysis of microliter blood samples can improve medical testing and forensics. Most critically ill patients suffer from hospital-acquired anemia due to the large volume currently required for blood diagnostic tests: 7 mL per vial.

Prior attempts by Theranos to analyze microliter-sized blood droplets in liquid form exhibit systematic errors greater than 10%, higher than the acceptable medical threshold.

This research investigates the accuracy of Ion Beam Analysis (IBA) performed on microliter-sized blood droplets congealed into Homogenous Thin Solid Films (HTSFs) using HemaDrop™, a new patent-pending technique using hyper-hydrophilic coatings to condense fluids into a uniform solid state with a smooth surface.

Prior to IBA analysis, the solidification of blood droplets into HTSF's is observed with optical microscopy and compared to conventional Dried Blood Spots (DBS). DBS exhibit phase separation between platelets and serum, with non-uniform, rough surfaces. Conversely, blood droplets solidified on HemaDrop™-coated surfaces are uniform and smooth, with little phase separation.

Next, quantitative compositional analysis using IBA is performed on µL blood drops solidified on HemaDrop™ coatings and is compared to results on DBS. HTSFs congealed on HemaDrop™-coated surfaces yield well-defined 2 MeV RBS spectra where individual species and electrolytes (C, N, O, Na, K, Ca, Cl, Fe) can be identified, while none can be distinguished on DBS.

The damage curve method [1] extracts elemental composition while accounting for possible IBA damage. Several consecutive spectra are taken on the sample, and RBS yields are interpolated to their original concentrations.

IBA simulations with the software SIMNRA enable comparison between RBS data and simulations, resulting in elemental composition accurate within 1%. Blood electrolyte compositions via SIMNRA are obtained on successive IBA spectra taken on different areas of the thin solid films and on different HTSFs congealed from the same blood. Relative error analysis between different HTSF samples establishes whether reproducibility within 10% can be achieved.

HemaDrop™ reliably creates stable, uniform, thin solid films to measure blood composition from µL-volume drops based on comparative IBA results and optical observations. Measurements of elemental composition of HTSF of blood samples are accurate and reproducible. HemaDrop allows for analysis in vacuo from µL of blood, greatly expanding the range of techniques that can be applied to identify elements and molecules (e.g., antibiotics, proteins).

[1] *Int & US Patent Pending, 2016, 2017

In-situ Microscopy, Spectroscopy, and Microfluidics Focus Topic

Room 202B - Session MM+AS+NS+PC+SS-MoA

X-ray and Electron Spectromicroscopy in Liquids and Gases & Flash Networking Session

Moderator: Piran Kidambi, Vanderbilt University

1:20pm **MM+AS+NS+PC+SS-MoA1 Bridging the Material and Pressure Gap in Synchrotron based Photoelectron in Situ/Operando Studies***, **Luca Gregoratti**, M. Amati, P. Zeller,* Elettra-Sincrotrone Trieste, Italy **INVITED**

Modelling the real behavior of technologically relevant materials at typical laboratory environmental conditions is a longstanding challenge. Not only classical pressure conditions are generally far from usual industrial environments (pressure gap) but also heterogeneous materials are very different from those often used to simplify the modelling strategies (material gap). For instance to monitor in-situ/operando the lateral distribution of the chemical state of surfaces and interfaces during a catalytic or electrochemical reaction at sub-micron level at environmental conditions as close as possible to the operational ones is of crucial importance to shed light on the running processes. But the possibility to investigate chemical reactions with X-ray photoelectron spectro-microscopies by overcoming material and pressure gaps is still a challenge also for modern experimental setups.

The Escamicroscopy team of Elettra which operates a Scanning Photoemission Microscope (SPEM) has recently developed novel concepts for a new generation of SPEM working under more realistic pressure conditions. The graphene sealed cells, combined for the first time with XPS by A. Kolmakov [1], allow the possibility to investigate systems which require an ambient pressure regime (e.g. liquid/solid interfaces). Despite the huge ongoing progress in the development and performance of these cells several crucial issues are unsolved and will be addressed by this presentation.

Another recent development is an effusive cell for near-ambient pressure SPEM setups where the highest static pressure achievable is around 1 mbar. Samples are encapsulated in a vacuum sealed cell and located behind a 200 µm diameter size pinhole through which the focused X-ray beam illuminates surfaces and photoelectrons reach the high vacuum path towards the electron analyzer [1].

2:00pm **MM+AS+NS+PC+SS-MoA3 Transition Metal Complexes in Aqueous Solutions Characterized by Liquid Jet Ambient Pressure X – ray Photoelectron Spectroscopy***, **Jared Bruce**, J.C. Hemminger,* University of California, Irvine

Transition metals in aqueous solution have been investigated by a multitude of techniques and are a cornerstone of many aspects of chemistry. Recently, the atmospheric chemistry community has begun to shift their attention to iron, manganese and copper containing aqueous solutions due to their propensity to generate hydroxyl radicals at the air/water interface through a Fenton mechanism. Understanding the chemical state of the transition metal present at the air/water interface, in addition to the distribution as a function of depth, would provide critical insight to the active species of hydroxyl generation. Solvation effects have been shown to significantly affect the distribution of small ions as a function of depth from the vacuum/water interface; first through molecular dynamics (MD) simulations then corroborated by liquid – jet X – ray photoelectron spectroscopy (LJ-XPS). Solvation of transition metals in aqueous solution have added complexity compared to small ions because of complexation of ligands and equilibria with the surrounding solvent.

In our work, using both a lab – based LJ - XPS and synchrotron measurements at the Advanced Light Source, we have shown the distribution of chemical states on a model Fenton reagent, $Fe^{2+}_{(aq)}$, change with depth relative to the air/liquid interface. The chemical state is also sensitive to “spectator” ions in the solution. The presence of Cl^- leads to a binding energy shift in the Fe 2p spectra and a change in the distribution as a function of depth. This is also observed in the Cl 2p spectrum where a binding energy shift of 0.3 eV indicates the presence of an inner sphere Cl that follows the distribution change in the Fe 2p spectrum

2:20pm **MM+AS+NS+PC+SS-MoA4 Interfacial Electrochemistry in Liquids Probed with Photoemission Electron Microscopy***, S. Nemsak,* Forschungszentrum Juelich GmbH, Germany*; E. Strelcov,* NIST Center for Nanoscale Science and Technology*; **Tomas Duchon**,* Forschungszentrum Juelich GmbH, Germany*; H.X. Guo,* National Institute of Standards and Technology*; J. Hackl,* Forschungszentrum Juelich GmbH, Germany*; A. Yualev,* NIST Center for Nanoscale Science and Technology*; I. Vlassiouk,* Oak Ridge National Laboratory*; D.N. Mueller, C.M. Schneider,* Forschungszentrum Juelich GmbH, Germany*; A. Kolmakov,* NIST Center for Nanoscale Science and Technology

The use of photoemission spectromicroscopy as a probe of liquid electrolytes has been an elusive goal, motivated by the breadth of information the technique can provide, but hindered by many technical difficulties. Here, we present a universal multichannel array platform employing graphene capping that allows for investigation of interfacial liquid electrochemistry via soft x-ray absorption and photoemission spectromicroscopy. The methodology is demonstrated in the case of copper electroplating from a sulphuric acid solution, that, along with cycles of copper deposition on gold electrodes, reveals hindered nucleation at the electrified graphene membrane evidenced by the presence of stable Cu+ ions.

3:40pm **MM+AS+NS+PC+SS-MoA8 Practical Liquid Cell Microscopy - Opportunities and Challenges***, **Daan Hein Alsem**, K. Karki,* Hummingbird Scientific*; J.T. Mefford, W.C. Chueh,* Stanford University*; N.J. Salmon,* Hummingbird Scientific **INVITED**

Transmission electron microscopy (TEM), scanning electron microscopy (SEM) and synchrotron X-ray microscopy (XRM) are powerful characterization tools and are routinely used to study a wide range of material-systems at the nanoscale. This has generated strong interests in acquiring more reliable quantitative *in-situ* and *operando* measurements in realistic reaction environments, as is possible with liquid environmental cells. This approach has already started to produce new insights on the dynamics and structural changes during electrochemical processes as lithium ion insertion/extraction, dendrite formation, metal nucleation and corrosion. However, practical aspects of replicating representative electrochemical data reminiscent of bulk behavior are still a challenge in these systems.

Here, we will discuss practical aspects of conducting *operando* liquid cell microscopy experiments relating to the typical geometry of these liquid-cell microscopy systems as well as artifacts coming from the microscope during *operando* experiments. We will also present a TEM/SEM/XRM microscopy platform that enables true electroanalytical measurements mimicking bulk behavior of the material system.

The example study shown here is performed using electrochemical cells, which consist of two microfabricated chips sandwiched with transparent SiNx membranes for encapsulating liquid and viewing in the microscope. A newly developed hardware system and specially optimized electrochemistry chips with a custom configuration for working electrode (WE), counter electrode (CE) and reference electrode (RE) allows quantitative measurements of electrochemical processes with details resembling the complete cycle of the bulk. As illustrations, we present cyclic voltammetry (CV) studies of some model compounds such as 01.M $CuSO_4$ and 20 mM $K_3Fe(CN)_6$/20 mM $K_4Fe(CN)_6$ in 0.1M KCl solutions. In the former case, the copper deposition and stripping occurs at the working electrode at distinct redox peaks in liquid cell and the result mimics the bulk electrochemical cells with large electrode areas and larger volume of electrolyte solution. This work highlights the fact that with suitable hardware systems and with knowledge and correction of microscope-induced artifacts, bulk behavior of the electrochemical processes can be both observed and measured quantitatively.

4:20pm **MM+AS+NS+PC+SS-MoA10 Observation of Electric Double Layer under Graphene by Scanning Electron Microscopy***, **Hongxuan Guo**, A. Yulaev, E. Strelcov,* National Institute of Standards and Technology (NIST)/ University of Maryland, College Park*; A. Tselev,* CICECO and Department of Physics, University of Aveiro,Portugal*; A. Kolmakov,* National Institute of Standards and Technology

The formation of the electric double layer is a fundamental phenomenon occurring at electrified solid-liquid electrolyte interfaces and which has a key importance for energy devices, chemical engineering and biomedical applications. The structure and composition of electric double layer can be accessed using optical methods [1], and more recently with X-ray spectroscopy [2, 3], as well as scanning probe microscopy[4].

In this presentation, we demonstrate the feasibility of *in-situ* scanning electron microscopy to observe the changes in electric double layer in different electrolytes upon polarization. We designed an electrochemical liquid cell with electron transparent electrode made of bilayer graphene.[5,6]. We monitored the changes in secondary electron yield from the graphene-liquid interface upon electrolyte polarization. We found that the normalized SEM image contrast is linear with the applied bias voltage and is related to the concentration and distribution of the ions at the interface. The analysis of SEM videos provide insight on long term kinetics of ionic moieties in electrolyte during polarization. This experimental methodology will be helpful for understanding the structure, property, and dynamics of the electric double layer at solid -electrolyte interfaces.

Reference

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Nanometer-scale Science and Technology Division
Room 102B - Session NS+2D+AS+PC-MoA

SPM - New Imaging and Spectroscopy Methodologies

Moderators: Aubrey Hanbicki, Naval Research Laboratory, Sidney Cohen, Weizmann Institute of Science, Israel

1:20pm **NS+2D+AS+PC-MoA1 A Connection Between Stability of STM Control System and Local Barrier Height: Implications on Imaging and Lithography***, **S.O. Reza Moheimani,*** University of Texas at Dallas **INVITED**

Poor performance of the Scanning Tunneling Microscope (STM) control system may result in tip-sample crash, a prevalent failure in STMs. Since its invention, about thirty-five years ago, few attempts have been made to improve the STM control system. Consequently, nearly all STMs are today operated with experimentally selected fixed-gain PI controllers. Selection of controller gains is often done without much attention to the electromechanical dynamics of the scanning tunneling microscope. Performance of such poorly-tuned controllers is limited and a key contributor to the tip-sample crash.

We perform closed loop system identification on a scanning tunneling microscope and show that the system DC gain is proportional to the square root of Local Barrier Height (LBH), a quantum mechanical property of the sample and/or tip that affects the tunneling current. We demonstrate that during a scan the LBH may undergo significant variations and thus it may adversely affect the closed-loop stability if the controller parameters are fixed. Feedback instabilities increase the risk of tip-sample crash in STMs.

In order to improve the closed loop performance, we estimate the LBH, on the fly, and use this information to adaptively tune the PI controller parameters. Experimental results obtained with the self-tuning PI controller confirm the improved STM performance compared to the conventional fixed gain PI controller. Further experiments confirm effectiveness of the proposed method in extending the tip lifetime by lowering the chance of the tip/sample crash.

2:00pm **NS+2D+AS+PC-MoA3 Distinctive Microstructures in a Complex Polymer Evolve with Time and Composition***, x. Yu,* Worcester Polytechnic Institute*; S. Granados-Focil,* Clark University*; M. Tao, **Nancy Burnham,*** Worcester Polytechnic Institute

The diverse microstructures observed by atomic force microscopy (AFM) in asphalt binder – a complex polymer – suggest complicated intermolecular associations. These microstructures contribute to binders' bulk mechanical properties; therefore, it is essential to understand chemical-microstructural-mechanical relationships for optimal design of binder-related applications, which range from roads to roofs. The US market for asphalt binders in 2019 is predicted to reach 148 million barrels. [1] Binders annealed at room temperature for over two months showed time-dependent microstructures, which correlate well with room-temperature steric hardening behavior as verified by other researchers using modulated differential scanning calorimetry. Microstructures of the binder films stabilized after different annealing durations, depending on the dimensions of the molecular structures and the complexity of the molecular interactions among the multiple phases in each bitumen. Distinctive microstructures were observed for remixed binders with increasing asphaltene concentrations. Consistency between our observations [2] and other literature suggests that microstructures observed by AFM are probably not just a surface phenomenon.

Furthermore, the complex nature of binder and the various influencing factors often lead to practical challenges in investigation of its microstructures and their chemical origins. Some of the main concerns related to AFM characterization of binders' microstructures, namely the dependence of the microstructures on such factors as sample preparation methods, annealing conditions and durations, and chemical composition, were also addressed in this study.

The above findings provide practical knowledge and deeper insights into the establishment of the complicated chemical-mechanical relationships for asphalt binders that pave the way toward tuned binder performance.

[1] https://www.reportlinker.com/p0158665/US-Asphalt-Industry.html

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2:20pm **NS+2D+AS+PC-MoA4 Offering new Characterization Capabilities at the XTIP beamline by Combining Scanning Tunneling Microscopy with Synchrotron Radiation***, **Volker Rose**, H. Chang, M. Fisher, S.W. Hla, N. Shirato,* Argonne National Laboratory

The race is on for chemical x-ray imaging with nanoscale resolution. Specifically, there are currently substantial efforts underway at synchrotron facilities worldwide that aim to combine x-rays with scanning probe microscopy. Recently, substantial progress was made on Argonne's Synchrotron X-ray Scanning Tunneling Microscopy (SX-STM) project. SX-STM enables an entirely new view into the nanoworld by combining the best of two worlds: the exceptional chemical, magnetic, and structural sensitivity of synchrotron x-rays combined with the high spatial resolution of scanning probe microscopy accompanied by its ability to engineer and manipulate surfaces down to the level of single atoms.

To fully exploit the special capabilities of a unique new cryogenic x-ray microscope, XTIP, a dedicated beamline for SX-STM will become available at the Advanced Photon Source in early 2019. To meet the scientific objective of the nanoscience and nanomagnetism communities most effectively, we are going to build a soft x-ray beamline with full polarization control operating over the 500-1600 eV energy range. The dedicated XTIP beamline will provide researchers access to a one-of-a-kind instrument. Among the potential breakthroughs are "designer" materials created from controlled assembly of atoms and molecules, and the emergence of entirely new phenomena in chemistry and physics.

2:40pm **NS+2D+AS+PC-MoA5 Scanning Probe Microscopy Based Spectroscopy Measurement for Nanoscale Chemical Identification***, **Chanmin Su,*** Bruker-Nano, Inc. **INVITED**

Scanning probe microscopy has been instrumental for physical property characterizations at the nanometer scale, primarily for mechanical, electromagnetic and thermal properties. Recent progresses were focused on chemical identification based on mid-IR spectroscopy, pushing FTIR mapping to a resolution at or beyond 10 nm. This presentation will review technology advances in both scanning near field optical microscopy and photothermal based IR spectroscopy. Each of the techniques is discussed and benchmarked by detection limit, spatial resolution and signal to noise ratio, which ultimately determines the chemical mapping efficiencies. We will highlight techniques that address correlative imaging where physical and chemical properties at the same nanoscale location being acquired either concurrently or sequentially. As an example, PeakForce tapping based chemical and physical measurements will be explained in detail with the applications ranging from 2D materials to polymer complexes. The presentation will also highlight major challenges for scanning probe based measurements to be broadly adopted as the premier tool for nanoscale chemical fingerprint mapping.

3:40pm **NS+2D+AS+PC-MoA8 Quantifying Tip-Sample Interactions in Vacuum Using Cantilever-based Sensors: An Analysis***, O.E. Dagdeviren, C. Zhou, E.I. Altman,* ***Udo D. Schwarz****,* Yale University

To achieve as much quantitative information on a surface as possible, the local measurement of tip-sample interaction potentials has recently gained much popularity in particular under well-defined ultrahigh vacuum conditions, where such measurements can be carried out with great accuracy both in terms of spatial as well as force resolution. To this end, either the oscillation frequency or the oscillation amplitude and phase of the vibrating force-sensing cantilever are recorded as a function of tip-sample distance and subsequently converted into quantitative values for the force or interaction potential. Here, we theoretically and experimentally show that the force law obtained from such data acquired under vacuum conditions using the most commonly applied methods may deviate more than previously assumed from the actual interaction when the oscillation amplitude of the probe is of the order of the decay length of the force near the surface, which may result in a non-negligible error if correct absolute values are of importance [1]. Caused by approximations made in the development of the mathematical reconstruction procedures, the related inaccuracies can be effectively suppressed by using oscillation amplitudes sufficiently larger than the decay length. To facilitate efficient data acquisition, we propose a novel technique that includes modulating the drive amplitude at a constant height from the surface while monitoring the oscillation amplitude and phase.Ultimately, such amplitude sweep-based force spectroscopy enables shorter data acquisition times and increased accuracy for quantitative chemical characterization compared to standard approaches that vary the tip-sample distance. An additional advantage is that since no feedback loop is active while executing the amplitude sweep, the force can be consistently recovered deep into the repulsive regime.

[1] O. E. Dagdeviren et al., Physical Review Applied **9**, 044040 (2018).

4:00pm **NS+2D+AS+PC-MoA9 AFM + Nanoscale Vis-IR Spectroscopy via Photo-induced Force Microscopy***,* ***Derek Nowak****, T. Albrecht, S. Park,* Molecular Vista

Photo-induced Force Microscopy (PiFM) [1] combines optical spectroscopy and atomic force microscopy (AFM) via illumination of the tip-sample junction with tunable laser light and mechanical detection of forces acting on the tip in response to interaction of light with the sample. With infrared (IR) source, PiFM can map the IR absorption of the sample as a function of IR wavelength and position and achieve nm-scale resolution in displaying the locations of heterogeneous materials on the surface of a sample. Even for samples without active IR absorption band, PiFM can be used to acquire nanoscale mapping based on the dielectric constant of the sample surface; dielectric constant mapping also allows high resolution sub-surface mapping. With tunable visible and near infrared (VisNIR) laser source, PiFM can map exciton resonances with similar spatial resolution even on monolayer samples. Examples from various classes of samples including organic, inorganic, and 2D materials will be presented. We will also present PiFM spectroscopy data that show excellent correlation with bulk FTIR spectra despite the fact that PiFM acquires local chemical information from regions in the range of 10 nm in extent.

[1] D. Nowak et al., Sci. Adv. **2**, e150157 (2016).

Applied Surface Science Division
Room 204 - Session AS+BI-TuM

Applied Surface Science: From Electrochemistry to Cell Imaging, a Celebration of the Career of Nicholas Winograd

Moderators: Arnaud Delcorte, Université Catholique de Louvain, Belgium, Michaeleen Pacholski, The Dow Chemical Company

8:00am **AS+BI-TuM1 Surface Analysis and Beyond, Using Ion Beams and Lasers***, **Nicholas Lockyer**, J.C. Vickerman,* University of Manchester, UK **INVITED**

Applications of secondary ion mass spectrometry (SIMS) have expanded enormously from pure surface science experiments to biology and bio-medicine, driven largely by developments in instrumentation. Polyatomic primary ion beams have resulted in a step-change in the technique's capability to detect and localise molecular chemistry, in biological cells and organic devices etc. This has stimulated new mass spectrometer designs and analytical paradigms for molecular imaging in 2D and 3D. The quest for still greater lateral resolution is a quest for improved sensitivity. Here ion beam chemistry can play a role, increasing the ionized fraction of the sputtered plume. Alternative routes to improved ionization and greater quantification include laser post-ionization. In this talk I will chart the progress made in these areas by our group in Manchester, and draw parallels with the work of the Winograd group, with whom we have had fruitful collaboration over many years.

8:40am **AS+BI-TuM3 A High Resolution Tandem MS Imaging Method to Probe the Composition of Organelles in Single Cells***, **Gregory L. Fisher**,* Physical Electronics*; C.E. Chini,* University of Illinois at Urbana-Champaign*; B. Johnson, M.M. Tamkun,* Colorado State University*; M.L. Kraft,* University of Illinois at Urbana-Champaign

A goal of cellular imaging is to ascertain the composition of organelles, e.g. lipid profiling or pharmaceutical efficacy. To date most MS imaging of organelles is accomplished by stable isotope labeling because the imaging ion beam produces primarily (di)atomic ions. Such analyses are void of desired molecular specificity. We employed a TOF-TOF imaging capability [2] to achieve molecular specificity and conjectured that an ER-Tracker stain would yield characteristic molecular ions with which to image the endoplasmic reticulum (ER) and ER tubules.

We used human embryonic kidney (HEK) cells that had a high number of ER tubules near the plasma membrane (PM). Experimental cells were transfected to express GFP-Kv2.1 fluorescent ion channels. The cells were stained with ER-Tracker which selectively labels the ER. Control specimens were neither transfected nor stained.

We observed by simultaneous MS imaging and tandem MS imaging, in both the positive and negative ion polarities, the atomic and molecular moieties characteristic of an ER-Tracker stain localized to the ER and ER tubule structures. The ion species used for tandem MS imaging of the ER and ER tubules, namely F^-, $C_6H_5^-$, $C_5H_5^+$ and $C_{17}H_{15}N_2O^+$, were shown irrefutably via the product ion spectra to arise solely from the ER-Tracker stain. Two-dimensional (2D) imaging revealed intersection of some ER tubules at the PM. Three-dimensional (3D) visualization via depth profile analysis, carried out to a depth of ≈ 40 nm from the PM, revealed additional ER tubules just under the PM. Some ER-Tracker was observed in the PM indicating ER tubule contact with the PM to form ER-PM junctions. We were able to confirm the presence and position of the PM owing to the presence of characteristic lipids, lipid fragments and fatty acids which were imaged in parallel. The observed tubule features were imaged at an effective lateral resolution of 137 nm and had measured diameters in the range of approximately 500 nm to 2 µm corresponding well with previous studies [3] and present total internal reflection fluorescence (TIRF) observations. More than a dozen control cells were analyzed, and neither atomic nor molecular moieties characteristic of the ER-Tracker were observed to be present. Our next aim is to visualize the ER within entire cells and to assess the lipid composition at different locations within the ER. By extension, with organelle-specific stains, we can apply this TOF-SIMS tandem MS imaging method to aspects of pharmaceutical delivery and metabolism.

9:00am **AS+BI-TuM4 SIMS and MALDI-MS. Competitive, Complimentary or Complementary Techniques for Bio-imaging?***, **John Stephen Fletcher**, I. Kaya,* University of Gothenburg, Sweden

Despite imaging SIMS being a much older technique than MALDI in the bio-MS imaging area MALDI has enjoyed considerably more widespread success. The advantage of higher resolution imaging that is possible with SIMS has generally been outweighed by the low signal for intact molecular ions that are routinely delivered by soft ionisation techniques like MALDI – and MALDI is cheaper. However, advances in ion beams and mass spectrometry for SIMS analysis in parallel with new matrices, sample preparation and analysis approaches for MALDI have brought the two techniques closer together with significant overlap in the 1-10 µm “small molecule” imaging range.

In this presentation the benefits (if any) of multimodal MS imaging are discussed using examples from cancer, cardiovascular and neurological studies. Analysis was performed using high energy (40 keV) gas cluster ion beams (GCIBs) for SIMS analysis on the Ionoptika J105 and different MALDI approaches including gentle/static MALDI on the Bruker Ultraflextreme. On tissue derivatisation strategies applicable to both techniques will also be presented.

9:20am **AS+BI-TuM5 High Spatial Resolution Metabolic Imaging using the 3D OrbiSIMS - Fundamentals of Metabolite Fragmentation and Biological Applications***, C. Newell, Y. Panina,* Francis Crick Institute, UK*; L. Matjacic, V. Cristaudo,* National Physical Laboratory, UK*; A.P. Bailey,* Francis Crick Institute, UK*; R. Havelund,* National Physical Laboratory, UK*; M. Yuneva, A.P. Gould,* Francis Crick Institute, UK*; **Ian S. Gilmore**,* National Physical Laboratory, UK

Ground-breaking advances in single-cell genomics and transcriptomics are revealing the heterogeneity of cells in tissue and are transforming biological understanding. There is a great need for metabolomics with single-cell resolution. Recent advances in both SIMS and MALDI imaging have pushed the spatial resolution boundary to a few micrometres [1-3].

Here, we report on the 3D OrbiSIMS [1] which combines a gas cluster ion beam (GCIB) that is able to simultaneously achieve a spatial resolution of < 2 µm with high mass resolving power (>240 k) and mass accuracies of ~1 ppm. The GCIB significantly reduces fragmentation of metabolites compared with small cluster ion beams and we provide fragmentation data for a variety of metabolites for different energy per atom conditions.

We demonstrate the OrbiSIMS capability with two biological examples. Firstly, a study of the cuticular lipid composition and distribution of drosophila and how these change with various environmental and genetic manipulations. Drosophila secrete many different classes of lipids to form a protective surface barrier against environmental challenges and hydrocarbons which play a separate role as pheromones that influence sexual behaviour. Secondly, to identify metabolic heterogeneity in mammary gland tumours. One of the hallmarks of cancer is deregulated metabolism, often characterised by increased glucose and glutamine uptake for energetic and anabolic purposes. Metabolic changes contribute to well-established tumour heterogeneity, which is a major challenge for anti-cancer therapeutics. We demonstrate a protocol to co-register high-resolution OrbiSIMS metabolite images with immunohistochemistry microscopy images of the same sample.

References

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2 Kompauer, M., Heiles, S. & Spengler, B. Autofocusing MALDI mass spectrometry imaging of tissue sections and 3D chemical topography of nonflat surfaces. *Nature Methods***14**, 1156, doi:10.1038/nmeth.4433 (2017).

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9:40am **AS+BI-TuM6 Small Molecule Imaging in Single Frozen-Hydrated Cells using High-Resolution Gas Cluster Ion Beam Secondary Ion Mass Spectrometry (GCIB-SIMS)***, **Hua Tian**, N. Winograd,* Pennsylvania State Univeristy

Cell heterogeneity leads to the development of antibacterial resistance and tumor relapses in response to drug treatment. Cell-to-cell differences have been extensively investigated at the DNA level. The study of rapid and dynamic small molecule fluctuations in single cells has lagged. However, the complete spectrum of biomolecules can be a direct indicator of cell phenotype and a reflection of immediate response to environment and chemical stress. There is currently no method to directly detect small molecules in their original state because of the rapid and dynamic nature of these molecules and impossibility of amplifying the metabolites. Previously, the characterization of drug and small molecules in cells are conducted using ensembles of cells, with which the spatial distribution, a vital piece for understanding biological processes is lost. The development of high resolution CCIB-SIMS in our lab has positioned us to directly image small molecule fluctuation in single cells under cryopreservation. The approach takes advantage of three aspects of GCIB-SIMS - low chemical damage, high yield of intact biomolecules, and the possibility of sub-micron lateral resolution. In this work, we utilize a DC beam buncher-ToF SIMS instrument to achieve high lateral resolution. Moreover, this configuration simplifies depth profiling since erosion and spectral acquisition are performed with a single beam. In addition, the flexibility of gas candidates for GCIB allows us to explore tailored beam for ionization enhancement, such as HCl, CH_4, CO_2 or H_2O (1~100%) doped Ar cluster beams. To illustrate this instrumental protocol, chemically resolved 3D images of single cells, HeLa cells and drug treated A549 (Carcinoma) and A673 (Ewing tumor) cells are imaged using a novel 70 keV $(CO_2)_{14000}$+ beam with a spot size of 1 µm. The stable intermediates from various biochemical pathways are visualized in single HeLa cells, demonstrating the sufficiency of the chemical sensitivity using GCIB. The drug propranolol is localized within the cellular structure of A673 and A549 cells, while no sign of fexofenadine is observed. This indicates that propranolol has high passive permeability in contrast to low passive permeability expressed by fexofenadine. Surprisingly, a lipid composition change is shown in A673 cells, particularly the depletion of phosphatidylinositol species after treatment. The approach provides a complete chemical picture of single cells at near original physiological and morphological state, opening the opportunities for single cell metabolomics and heterogeneity studies using SIMS.

11:00am **AS+BI-TuM10 Pushing the Limits of Measurement Science with SIMS***, **Christopher Szakal**, D.S. Simons, J.D. Fassett, T.P. Forbes,* National Institute of Standards and Technology (NIST) **INVITED**

The career of Dr. Nicholas Winograd was exemplified by an unwillingness to accept the scientific status quo. Both in words and actions, he set a tone that encouraged everyone he worked with to ‘push the limits’ of what they thought was possible within their research endeavors. In this presentation, several topics will be explored where this mindset has been directly put into practice. A mix of historical examples, recent advancements, and new science that fit within the theme will be presented. Specifically, topics related to cluster ion beams, single cell imaging, single cell quantification, precision isotopic measurements, secondary ion mass spectrometry (SIMS) standard generation, and precision atmospheric pressure ionization MS measurements will be described in terms of how the measurement science boundaries were assertively targeted. Since Dr. Winograd had a fondness for cutting-edge instrumentation throughout his career, the presented efforts will focus on pushing the limits within time-of-flight (TOF)-SIMS, large geometry (LG)-SIMS, and ultra-high-resolution (UHR)-MS quadrupole(Q)-TOF technologies.

11:40am **AS+BI-TuM12 Multiplexed Ion Beam Imaging: Cell and Tissue Imaging using Secondary Ion Mass Spectrometry for Pathology***, **Jay Tarolli**, R. Finck, M. Aksoy, D. Stumbo,* Ionpath, Inc.

Traditional techniques for protein imaging in tissue sections based on light microscopy are limited in the number of simultaneous targets that can be analyzed in a single sample. The need exists in pathology, however, for concurrent imaging of more than just a few of these biomolecules to determine localization of cell types in tissue biopsies. Multiplexed ion beam imaging (MIBI) uses secondary ion mass spectrometry (SIMS) to overcome these limitations and is capable of imaging over 40 biomolecules simultaneously with a spatial resolution greater than many traditional optical and fluorescence microscopy techniques.

In a typical MIBI analysis, a tissue sample is stained with target antibodies conjugated to isotopically pure lanthanide metals. The resulting mass spectra of monoatomic heavy metals exhibit a more characteristic response than the complex mass spectra of fragmented biomolecules typically acquired when analyzing tissue samples with SIMS, the benefit of which being twofold: First, as ion counts from the target analytes are preserved instead of lost due to fragmentation into uncharacteristic species, the generated images have a higher signal to noise ratio. Secondly, now that fragmentation of target analytes is not a limitation, a high current primary ion beam with a tight focus can be employed to image tissue samples with a high spatial resolution at a high throughput rate. Specifically, an oxygen duoplasmatron primary ion beam, focusable down to a spot size of 350 nm, is used in conjunction with a time-of-flight mass analyzer to enable to the simultaneous detection of more than 40 labels at a resolution where individual cells can be differentiated in tissue samples.

12:00pm **AS+BI-TuM13 Combined ToF-SIMS and AFM Protocol for Accurate 3D Chemical Analysis and Data Visualization***, **Maiglid Andreina Moreno Villavicencio**, N. Chevalier, J.-P. Barnes, I. Mouton,* Univ. Grenoble Alpes, CEA, LETI, France*; F. Bassani,* Univ. Grenoble Alpes, CNRS, LTM, France*; B. Gautier,* Université de Lyon, INSA Lyon, Institut des Nanotechnologies de Lyon, UMR CNRS 5270, F- 69621 Villeurbanne cedex, France

In dual-beam time-of-flight secondary ion mass spectrometry (ToF-SIMS) depth profiling, a succession of two-dimensional chemical images is acquired. The provided images can be used to generate a three-dimensional (3D) visualization of the sputtered volume. However, standard reconstruction methods do not take into account the initial sample topography or lateral variations in sputter rates.

Due to geometry and the diversity of materials the resulting 3D chemical visualization of heterogeneous and non-planar samples may be distorted. To address this issue ToF-SIMS analysis was combined with atomic force microscopy (AFM). This combination supplies the missing sample topography of the ToF-SIMS images and allows the calculation of sputter rates for the materials present in the sample.

To achieve an accurate 3D ToF-SIMS reconstruction a protocol was developed that combines AFM topographical images, crater depth measurements and sequences of ToF-SIMS images, all acquired on the same area of the sample. This combined ToF-SIMS/AFM methodology was applied to a sample consisting of GaAs selectively grown in SiO_2 patterned structures using MOCVD. The initial topography revealed that the GaAs areas were higher than SiO_2 patterns, and the large sputter rate differences (up to a factor 2) mean that a simple reconstruction (flat surface and constant sputter rate) leads to severe distortions in the 3D ToF-SIMS reconstruction.

Using the combined methodology, a 3D overlay between AFM and ToF-SIMS images at each interface can be made and the local sputter rate can be mapped. Finally, a protocol was developed for the correction of the 3D ToF-SIMS reconstruction and depth-profiles within a rendered volume defined by successive AFM imaging.

This work was carried out on the nanocharacterisation platform (PFNC) of the CEA Grenoble and this project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 688225.

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Industrial Physics Forum
Room 101B - Session IPF+AS+BI+MN-TuM

Advanced Imaging and Structure Determination of Biomaterials

Moderators: David G. Castner, University of Washington, Michael Grunze, Max Planck Institute for Medical Research

8:00am **IPF+AS+BI+MN-TuM1 Chemical Imaging as a Tool to asses Molecular and Morphologic Content in Natural Tissues and Fabricated Models***, R. Bhargava, T. Comi, M. Gryka, **Kevin Lee Yeh**,* University of Illinois at Urbana-Champaign **INVITED**

Chemical imaging, in which molecular content is obtained using spectroscopy and images are formed using microscopy, is an emerging area to characterize cells and tissues. We present here a chemical imaging approach based on mid-infrared spectroscopic imaging that combines the spatial specificity of optical microscopy with the molecular selectivity of vibrational absorption spectroscopy. IR spectroscopic imaging is particularly attractive for the analysis of cells and tissue in that it permits a rapid and simultaneous fingerprinting of inherent biologic content, extraneous materials and metabolic state without the use of labeled probes. Recorded data are related to the structural and functional state of the biological material using computation. We describe the computational strategy and statistical considerations underlying decision-making for this modality. A combination of theory, novel instrumentation and signal processing forms an integrated approach to biochemical analyses. First, we describe attempts to automate histopathology without dyes or human input. Results indicate that a rapid assessment of tissue is possible. Applied to engineered 3D tissue models for breast tumors, we show that the imaging technology is useful in rapidly assessing culture quality and that the model systems can act to inform researchers about the involvement of different cell types in cancer progression. Finally, we integrate imaging observations with those from conventional biological experiments to provide a complete view of cancer progression in these systems.

8:40am **IPF+AS+BI+MN-TuM3 Fluorescence Dynamics and Nonlinear Optical Imaging Methods for Biomedical Applications***, **Alba Alfonso Garcia**, L. Marcu,* University of California at Davis **INVITED**

Generation of quality bioengineered tissue constructs, a main cornerstone for regenerative medicine, require new tools to monitor their maturation processes. Optical imaging, and in particular fluorescence dynamics and nonlinear optical techniques, provides the means for non-destructive, longitudinal, and quantitative evaluation. Using fiber optics and catheterized imaging systems these strategies are implemented with flexible geometries that allow investigations be performed outside of the realm of the microscope and the microscope slide, but instead *in situ*, on bioreactors, culturing wells and chambers, or even *in vivo*. Fluorescence dynamics and nonlinear optical imaging are especially well suited as they rely on intrinsic properties of the biomaterials to generate contrast. Tissue autofluorescence allows spectroscopic evaluation of tissue components, and the analysis of its temporal dynamics leads to functional analysis of tissue status. Additionally, nonlinear light-matter interactions probe vibrational and electronic energy levels that provide enhanced biochemical specificity of tissue constituents. All these approaches are compatible with label-free strategies, avoiding the addition of labeling agents onto already complicated samples. In this presentation, I will overview applications of fluorescence dynamics and nonlinear optical imaging including fluorescence lifetime imaging, two-photon fluorescence or second harmonic generation in tissue engineering. In particular, I will discuss tracking approaches to visualize recellularization processes on bioengineered vascular constructs. I will also characterize tissue composition of carotid arteries along their length based on their autofluorescence lifetime signals, and how this correlate with the structural protein composition of the vessel wall as evaluated by gold-standard biochemical assays. Finally, we will see how these methods are also applied in different fields such as the generation of cartilage-based implants, and the real-time discrimination of healthy versus diseased tissues in the context of cancer diagnostics.

9:20am **IPF+AS+BI+MN-TuM5 Single Molecule Imaging of Receptor Signalling***, **Katharina Gaus**,* University of New South Wales, Australia **INVITED**

Antigen recognition by the T cell receptor (TCR) is a hallmark of the adaptive immune system. When the TCR engages a peptide bound to the restricting major histocompatibility complex molecule (pMHC), it transmits a signal *via* the associated CD3 complex. How the extracellular antigen recognition event leads to intracellular phosphorylation remains unclear.

We develop single-molecule localization microscopy (SMLM) apporaches and novel analysis to determine how spatial organization regulates signal initiation and propagation. For example, we used SMLM data to map the organization of TCR-CD3 complexes into nanoscale clusters and to distinguish between triggered and non-triggered receptor copies. We found that only TCR-CD3 complexes in dense clusters were phosphorylated and associated with downstream signaling proteins, demonstrating that the molecular density within clusters dictates signal initiation. This lead us to propose a model in which antigen recognition is first translated into receptor clustering and then the density of receptor nanoclusters is translated into signaling. This model may explain how T cells can respond to both the affinity and dose of pMHC molecules with a common signal transduction mechanism (Pageon et al. PNAS 2016). We also developed novel FRET sensors to monitor the rate of receptor clustering (Ma et al. Nat Commun 2017) and a sensor that reports membrane charges (Ma et al. Nat Biotech 2017) to understand how biophysical properties of the plasma membrane contribute to TCR signaling.

11:00am **IPF+AS+BI+MN-TuM10 Developing a Google-earth View of Tumour Metabolism through Multiscale Molecular Imaging***, J. Bunch, **Rory T. Steven**,* National Physical Laboratory, UK **INVITED**

Mass spectrometry (MS) is one of the most powerful techniques for chemical analysis and when combined with an imaging modality allows molecular chemistry to be visualised in 2D and 3D, from the nano- to the macroscale, in ambient conditions and in real-time. There are numerous techniques each having different modes of operation including label-free and labelled analyses.

Cancer Research UK has identified that building an understanding of the inter- and intra- heterogeneity of tumours and their evolution over time and in response to therapy will require greater insight into the underlying biology, using *in vivo* and *in vitro* models and integrating biomarkers into both early- and late-phase trials. In 2017 the Grand Challenge programme was launched. Our collaborative action involves NPL, Imperial College London, The Beatson Institute, ICR, Barts Cancer Institute, The Francis Crick Institute, The University of Cambridge and AstraZeneca. Together we will develop a validated pipeline for multi-scale imaging of tumours collected from GEMMs and patients.

By pursuing a multiscale (organ to organelle) and multi-omics approach with a range of mass spectrometry imaging (MSI) techniques (MALDI, DESI, SIMS and ICP MS), we aim to deepen our understanding of the interplay of genes, proteins, metabolites and the role of the immune system in cancer development and growth.

This presentation will review early results and a discussion of the challenges associated with such a large, multi-technique, multi-site, mass spectrometry project.

11:40am **IPF+AS+BI+MN-TuM12 X-ray Diffraction and Coherent Imaging with Nano-focused Radiation: A Multi-scale Approach from Biomolecular Assembly to Cell, Tissue and Organ***, **Jan-David Nicolas**, T. Salditt,* University of Göttingen, Germany **INVITED**

X-rays deeply penetrate matter and thus provide information about the functional (interior) architecture of complex samples, from biological tissues and cells to novel composite materials. However, this potential of hard x-rays in view of penetration power, high spatial resolution, quantitative contrast, and compatibility with environmental conditions has to date not been fully developed, mainly due to significant challenges in x-ray optics. With the advent of highly brilliant radiation, coherent focusing, and lensless diffractive imaging this situation has changed. We show how nano-focused hard x-rays can be used for scanning as well as for full field holographic x-ray imaging of biological samples [1]. The central challenge of inverting the coherent diffraction pattern will be discussed and different reconstruction algorithms will be presented, from holographic techniques [2] to ptychography [3,4]. Next, we will present new approaches to treat the massive diffraction data recorded in scanning nano-diffraction experiments of cells and tissues [5].

By scanning the sample through the focused x-ray beam and recording full diffraction patterns in each scan point, structural parameters can be mapped throughout the cell or histological section [6], offering a 'diffraction contrast' by which one can localize also unstained biomolecular assemblies in cells and tissues, and at the same time investigate their structure. As an example, we address the sarcomeric organization in heart muscle cells (cardiomyocytes) [7,8], and show how the sarcomere organization evolves and differs between different cell types and maturation states. As a multi-scale approach, we then discuss sarcomeric structure in heart tissue sections, and then finally present phase contrast tomography reconstructions of an entire mouse heart.

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Processing and Characterization of Air-Liquid, Solid-Liquid and Air-Solid Interfaces Focus Topic

Room 202A - Session PC+AS+BI+NS+PB+SS-TuM

Solid-Liquid and Gas-Liquid Interfacial Processes and Characterization

Moderators: Stephen Nonnenmann, University of Massachusetts - Amherst, Juan Yao, Pacific Northwest National Laboratory

8:00am **PC+AS+BI+NS+PB+SS-TuM1 Liquefied Gas Electrolytes for Electrochemical Energy Storage Devices***, Y.S. Meng,* University of California San Diego*; **Yangyuchen Yang,*** University of California at San Diego **INVITED**

Electrochemical energy storage devices, such as Li-ion batteries and electrochemical capacitors, have seen little change in their electrolyte chemistry since their commercialization. These liquid electrolytes often limit the energy density and low-temperature operation of these devices, which hinder many potential applications. Our work uses electrolytes based on solvent systems which are typically gaseous under standard conditions and show excellent performance in electrochemical energy storage devices. It has demonstrated that these novel solvents have superior physical and chemical properties which are attributed to excellent performance over an extended temperature range and a wide potential window of stability with unique safety features. The use of fluoromethane as solvent for lithium batteries shows excellent low-temperature operation down to -60 °C with high capacity retention. The liquefied gas electrolytes also show a high coulombic efficiency for cycling dendrite-free lithium metal anodes.

8:40am **PC+AS+BI+NS+PB+SS-TuM3 An *In situ* Molecular-scale View of Nucleation and Self-assembly at Solid-liquid Interfaces***, **James De Yoreo,*** Pacific Northwest National Laboratory **INVITED**

Nucleation and self-assembly from solutions are seminal processes in the formation of ordered structures ranging from simple inorganic crystals to macromolecular matrices. Observations over the past fifteen years have revealed a rich set of hierarchical nucleation pathways involving higher-order species ranging from multi-ion clusters to dense liquid droplets, as well as transient crystalline or amorphous phases. Despite their complexity, a holistic framework for understanding particle-based pathways to crystallization that extends classical concepts emerges when the coupled effects of complexity of free energy landscapes and the impact of dynamical factors that govern particle formation and interaction are considered.Here I use a series of in situ TEM and AFM studies on inorganic, organic, and macromolecular systems to illustrate that framework via the evolution in nucleation and growth processes as these complexities and dynamical factors come into play. The results show that the introduction of either size-dependent phase stability associated with the high surface-to-volume ratios of nanoparticles, or high driving force coupled with the existence of metastable polymorphs leads to two-step pathways characterized by the initial appearance of a bulk precursor phase. The creation of micro-states, which represent local minima in free energy stabilized by configurational factors associated with structural elements of molecules, can also lead to hierarchical pathways, but the intermediates are microscopic transient states that do not appear on a bulk phase diagram. However, small changes in molecular structure can eliminate these transient states, leading to a direct pathway of nucleation.Limitations on molecular mobility, either through large barriers to changes in coordination or conformation, reduced temperature, or introduction of ion-binding polymers, can freeze non-equilibrium states into place for dynamical reasons. Analysis of sub-critical cluster evolution and subsequent nucleation shows that these dynamical constraints can lead to density fluctuations in accordance with classical descriptions even when non-classical pathways dominate.The findings from these in situ studies provide a common basis for understanding the development of order in systems as diverse as simple salt crystals, branched semiconductor nanowires, and microbial membranes.

9:20am **PC+AS+BI+NS+PB+SS-TuM5 Non-linear Surface Spectroscopy at the Aerosol Particle/Gas Interface***, Geiger, **Ariana Gray Be,*** Northwestern University **INVITED**

While the interface of the aerosol gas and particle phase is the first entity encountered by incoming gas phase species, accessing it with bond-specific methods has been hindered due to a lack of tools that can operate under ambient pressure and temperature conditions. Here, we overcome this hurdle by using nonlinear optics and demonstrate the utility of vibrational sum frequency and second harmonic generation for probing the surfaces of sea spray aerosol, secondary organic aerosol, and anthropogenic influence on them. By following the heterogeneous physical and chemical processes that drive gas-to-particle conversion, aerosol formation, their transformations and phase transitions, and reactivity, we provide the molecular origin for cloud activation.

11:00am **PC+AS+BI+NS+PB+SS-TuM10 The Influence of Electrochemical Potential and Water Vapor on Ionic Liquid Binding Energy Shifts Examined by AP-XPS***, **Meng Jia,*** Unversity of Delaware*; A. Broderick, J.T. Newberg,* University of Delaware

Ionic liquids (ILs) have relatively high electrochemical and thermal stability, good conductivity and low volatility, making them inherently “greener and safer” compared to the conventional electrolytes. The application of ILs in the field of electrochemistry has identified many opportunities for their use as electrolytes in electrochemical devices. 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. Ambient pressure X-ray photoelectron spectroscopy (AP-XPS) is sensitive to both the chemical and electrical states of materials, which makes it an ideal method for studying surface potentials in electrochemical devices. In this work we examine the IL-gas interface of 1-butyl-3-methylimidazolium acetate, [BMIM][OAc], deposited on an Au foil via AP-XPS as function of electrochemical potential and surrounding water vapor pressure. The electrochemically induced binding energy shifts (ΔBE/ΔE) of carbon, nitrogen, and oxygen species of the IL were analyzed. Results reveal that in the absence of water vapor there is an ohmic drop between the electrode-IL interface and the IL-vacuum interface, giving rise to a ΔBE/ΔE value of less than one. Upon introducing water vapor, forming an IL/water mixture, the ΔBE/ΔE approaches a value of one as a function of increasing pressure. We attribute this behavior to a decrease in the ohmic drop as the IL/water mixture becomes more conductive. These results suggest that the electrochemical potential of the IL-gas interface is influenced by both an external bias and by varying the surrounding relative humidity. The same is likely true for the IL-electrode interface where water is known to be present.

11:20am **PC+AS+BI+NS+PB+SS-TuM11 Role of Air Gas at the Interface between Water and Graphite Surfaces***, **Ing-Shouh Hwang,*** Institute of Physics, Academia Sinica, Taiwan, Republic of China*; C.W. Yang, C.K. Fang,* Institute of Physics, Academia Sinica,Taiwan, Republic of China*; Y.H. Lu,* Institute of Physics, Academia Sinica, Taiwan, Republic of China*; H.C. Ko,* Institute of Physics, Academia Sinica,Taiwan, Republic of China

The saturation concentrations of nitrogen and oxygen in water under ambient conditions are very small (~10 ppm), thus their roles have been largely ignored. Using advanced atomic force microscopy, we study the evolution of gas-containing structures at graphite/water interfaces at room temperature. Our study indicates that gas (mainly nitrogen and oxygen) molecules dissolved in water tend to adsorb onto hydrophobic/water interfaces [1]. In gas-undersaturated water, we observe gradual nucleation and growth of small two-dimensional (2D) ordered domains over time on graphite surfaces [2]. The ordered structures may eventually cover the entire interface. When water is gas-supersaturated or when fresh DI water is briefly heated, we observe cap-shaped fluid nanostructures in addition to the ordered domains [3]. The cap-shaped nanostructures are the so-called interfacial nanobubbles (INBs) or surface nanobubbles, whose nature, stability, and formation remain controversial. When water is slightly gas-supersaturated, we see evolution of the fluid-like structures. The fluid phase first appears as a circular wetting layer ~0.3 nm in thickness and is later transformed into a cap-shaped INB [4]. 2D ordered domains are nucleated and grow over time outside or at the perimeter of the fluid regions, eventually confining growth of the fluid regions to the vertical direction. We determined that INBs and the fluid layers have very similar mechanical properties, suggesting low interfacial tension with water and a liquid-like nature.

Our study suggests that, in gas-undersaturated water, dissolved gas molecules may mainly be in the dispersed monomer form. Their rearrangement with water molecules at hydrophobic/water interface may lead to gradual nucleation and growth of the ordered domains. In gas-supersaturated water, some dissolved gas molecules are well dispersed in water, but others may aggregate into clusters. Adsorption of gas clusters leads to the formation of circular fluid layers at the graphite/water interface. The work clearly shows the crucial role of gas molecules at hydrophobic/water interfaces and has broad implications in diverse research fields.

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11:40am **PC+AS+BI+NS+PB+SS-TuM12 Probing Cluster and Nanoparticle Growth Processes with X-Ray Spectroscopy and Mass Spectrometry*, Musahid Ahmed,*** *O. Kostko,* Lawrence Berkeley National Laboratory **INVITED**

Tunable synchrotron radiation (VUV and X-rays) provides a universal, yet selective scalpel to decipher molecular information in complex chemical systems when coupled to mass spectrometry and X-Ray spectroscopy. This provides profound insight into molecular growth mechanisms, solvation and electronic structure in clusters, complexes and nanoparticles. In the first part, I will describe how single photon ionization mass spectrometry may be applied to molecular beams to probe molecular growth that is mediated either by ion or neutral pathways. The association and dissociation pathways in acetylene clusters where bonding can change from van der Waals to covalent upon ionization leading to the formation of benzene will be described.[1] I will follow up with very recent results on association of water with "hydrophobic" naphthalene & "hydrophilic" glycerol where subtle non covalent interactions can lead to surprising results in electronic structure and its effect on the hydrogen bonding network of water.

X-ray spectroscopy provides a local probe of a sample's electronic structure with elemental and site-specificity and is thus ideally suited for probing solvation. Since X-rays can probe surfaces, interfaces and bulk, and more important penetrate matter, it provides for interrogation of buried and confined spaces. Here I will describe a new approach, Velocity Map Imaging X-Ray Photoelectron Spectroscopy coupled to nanoparticle beams[2] that allows for the visualization of dynamic processes in solvation and molecular growth processes. I will describe its' implementation on aqueous arginine aerosols, where by varying the pH of the constituent solution, evidence is provided that the guanidinium groups are protonated even in a very basic solution (pH 13).[3] A molecular level picture of how charge and proton transport in aqueous solutions of arginine occur emerges by analyzing the energy shifts on the C and N X-ray photoelectron spectra. I will conclude by suggesting new approaches to probe gas liquid interactions and chemistry with X-Ray spectroscopy and microfluidic devices allowing access to liquids in vacuum.[4]

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Thin Films Division
Room 102A - Session TF+AS-TuM

Special Session in Honor of Paul Holloway: Luminescent Materials Growth, Synthesis and Characterization

Moderators: Sean Jones, National Science Foundation (NSF), Jay Lewis, Defense Advanced Research Projects Agency

8:00am **TF+AS-TuM1 INTRO: Special Session Honoring Professor Paul H. Holloway*, Gary McGuire,*** Adamas Nanotechnologies

In light of Professor Holloway's many contributions to the AVS and Thin Film Division special recognition will be given to him during a session dedicated to highlighting his prominence as an educator, scientist and leader. Professor Holloway has held many positions within the AVS including AVS President in 1987, Fellow 1993, Honorary Member 1997, Albert Nerken Award Winner, 1999. The Paul H. Holloway Young Investigator Award is given each year by the Thin Film Division to a deserving recipient. During his career he made major contributions to surface science and surface analysis. His research covered a diverse range of luminescent materials including thin film and powder phosphors, organic light emitting diodes, quantum dots and nanocrystals.

8:20am **TF+AS-TuM2 Harnessing Disorder in Detectors*, Jay Lewis,*** Defense Advanced Research Projects Agency

Most progress in optoelectronic devices has been built upon increasingly perfect materials, where "perfect" implies reducing impurities, point defect, dislocations, and grain boundaries. However the properties of quantum dot devices, such as those demonstrated by the Holloway group, are largely dominated by the surfaces of the nanocrystals. This paper explores the role of nanostructured devices through the lens of DARPA's Wafer Scale Infrared Detectors (WIRED) program, which seeks to develop infrared detector technology that is inherently disordered. Disorder is a byproduct of the program objective to process detectors directly onto the silicon wafers that are used to process and read out the signals. The program is exploring polycrystalline materials deposited by chemical bath deposition, quantum dot materials deposited by spin or dip coating, as well as traditional III-V compounds deposited at low temperatures compatible with complementary metal oxide semiconductor (CMOS) circuitry. These results are presented in the context of the broader portfolio of DARPA programs seeking to advance the state of the art in imaging and sensing technology.

8:40am **TF+AS-TuM3 Luminescent Materials for Solid State Lighting and Solar Cell Applications*, Hendrik C Swart,*** *J.J. Terblans, R.E. Kroon, E. Coetsee, M.M. Duvenhage, E. Hasabeldaim, A. Balakrishna, A. Kumar,* University of the Free State, Republic of South Africa*; P.H. Holloway,* University of Florida **INVITED**

Luminescent compounds and materials have numerous uses. The emission properties, whether of a fast decay rate fluorescent material or a slow decay rate phosphorescent material, are defined by the chemical composition and the physical structure of the luminescent material. The crystal field that is determined by the environment in the host material in combination with the various dopant ions with the correct valence state can be used to obtain emissions from the Ultra violet (UV) to the infra-red (IR) wavelength ranges. Phosphor materials have been successfully used to improve the efficiency of various applications. Nanoparticles both undoped and doped with different rare earth elements were synthesized by several synthesized techniques. The major problem that limits solar cells' efficiency is their insensitivity to the whole solar spectrum which is the so-called spectral mismatch. Therefore, several mechanisms have been explored based on photoluminescence (PL) to convert the solar cell spectrum where the spectral response of the solar cell is low to regions where the spectral response of the solar cell is high. For single crystalline silicon (Si) photovoltaic (PV) cells with a rather small semiconductor band-gap (Eg: 1.12 eV, corresponding to a wavelength of ~1100 nm), the transmission loss of the sub-band-gap photons can still amount to about 20% of the sun's energy irradiated onto the Earth's surface. For PV cells with a larger band-gap, such as amorphous Si (Eg: 1.75 eV) solar cells, which are limited to absorb sunlight with wavelengths below 708 nm, manifest even higher near infrared transmission losses. Downconversion, up-conversion (UC) and downshifting are some of the mechanisms that may be applied to improve the spectral response. Upconversion nanoparticles (UCNPs) have shown some promising possibilities to be considered in this respect, however, low UC efficiency of UCNPs is still the most severe limitation of their applications. In downshifting the strong deep level emission (DLE) and near band edge emission could be tuned to cover a wide spectral range. The strong DLE, covering a wide spectral range of ~375-650 nm, signifies the potential optoelectronics application in the near white LED applications. Degradation of the different phosphors during prolonged electron/photon bombardment also played a vital role in their possible applications. Examples of different phosphor materials with different applications such as Solid State Lighting will be shown.

9:20am **TF+AS-TuM5 Fluorescent Nanodiamond for Applications in Whole Body Imaging*, Olga Shenderova,*** *M.D. Torelli,* Adamas Nanotechnologies*; A. Rickard,* Duke University*; N.J. Nunn,* Adamas Nanotechnologies*; M. Backer,* SibTech*; G.M. Palmer,* Duke University*; G. McGuire,* Adamas Nanotechnologies **INVITED**

Fluorescent nanodiamonds (FNDs) containing color centers exhibit distinct properties including very high biological compatibility, infinite photostability, absence of photoblinking, long fluorescence lifetime (>10 ns), and ease of biofunctionalization, which makes them an attractive alternative to quantum dots, organic dyes, and polymer beads as imaging reagents. Potential applications include background-free and long-term cell imaging, flow cytometry, super-resolution imaging, correlative microscopy, labeling of low-abundance cellular components, fiducial markers, and image guided surgery. In this talk, after reviewing unique properties of FND, their utility for in vivo tumor imaging will be presented. To target receptors overexpressed in cancerous tissue, FNDs were functionalized with vascular endothelial growth factor (VEGF) via click chemistry and then validated *in vitro* for functional activity. Thereafter, FND-VEGF was administered via tail vein injection to nude mice induced with a mammary carcinoma, and mice were analyzed both in vivo and ex vivo via whole body imaging and fluorescence microscopy. Ex vivo micro-spectroscopy utilized the unique spectral signature of nitrogen-vacancy induced fluorescence to demonstrate unambiguous determination of ND translocation to tumorous tissue. The results are placed in the context of FND for whole-body imaging and related applications.

11:00am **TF+AS-TuM10 The Apple does not Fall Far from the Tree: A Serendipitous Journey from Luminescent Materials to Nanoscale Focused Electron (and Ion) Beam Induced Processing***, **Philip D. Rack**,* University of Tennessee Knoxville **INVITED**

I graduated from Paul Hollloway's group at the University of Florida in 1997 where I studied luminescent materials for electroluminescent displays. If the saying is true that "imitation is the sincerest form of flattery," then my career speaks volumes of my admiration for the man I had the privilege to call my Phd advisor. In this talk, I will briefly overview some of the luminescent materials research that my group has performed over the years. In true Holloway fashion, I will overview my groups serendipitous journey from luminescent materials to focused nanoscale electron beam induced processing. The remainder of the talk will review topics near and dear to Dr. Holloway's heart, electron(ion)-gas-solid interactions, and illustrate that appropriate understanding of these interactions can result in the directed growth/etching at the nanoscale. I will overview our groups Monte Carlo simulation to illustrate some of the critical electron(ion)-gas-solid interactions that can rate and resolution limit the deposition and etching processes. Next, I will show how a synchronized pulsed laser can photothermally assist both the etching and deposition processes. Finally, I will review our recent research direction in this area, which is controlled 3d nanoscale printing. Along the way, I will recall anecdotes that illustrate principles learned from the "Holloway way" and hopefully illustrate that I am an apple that did not fall far from the Holloway tree.

11:40am **TF+AS-TuM12 Atomic Layer Deposition of Optoelectronic Materials***, **Markku Leskela**, M.K. Ritala,* University of Helsinki, Finland **INVITED**

In optoelectronics, i.e. in electronic devices and systems that emit, detect and control light, the active materials are usually II-VI or III-V semiconductors. Historically in Atomic Layer Deposition (ALD) or Atomic Layer Epitaxy (ALE) as it was called in 70s and 80s, zinc sulfide has been very important material. The ALE technology was developed for manufacturing AC driven thin film electroluminescent displays [1]. Monochromic yellow-black displays based on ZnS:Mn luminescent layer sandwiched between dielectrics and electrodes has been manufactured industrially by ALD continuously since 1984. Besides the luminescent layer, the high-quality oxide layers made by ALE have had an important role as dielectrics and passivation layers in the success of the ACTFEL displays. Multicolor displays can be realized by filtering the broad emission band of ZnS:Mn or using other luminescent material, e.g. green-emitting ZnS:Tb. Despite of intense studies in 1980s and 1990s full-color ACTFEL devices could not been developed to the mass production level because of the missing efficient deep blue-emitting phosphor. Today the strongest developing application area in thin film EL displays is transparent displays used widely in different vehicles [2]. This motivates to re-examine the color displays.

Deposition of epitaxial films of III-V materials is possible with ALD as demonstrated already in 1985 [3]. Processes have been developed for all III-V materials using alkyl compounds for group III metals and hydrides for group V elements as precursors. The advantages of ALD processing compared to MOCVD or MBE have remained, however, modest because of the carbon contamination.

Transition metal dichalcogenides are emerging 2D materials that are potential channel materials in field-effect transistors as well as phototransistors and other optoelectronic devices. The bottle-neck in the large use of these two-dimensional materials is the lack of scalable, low-temperature process for high-quality, large-area films. ALD has been studied as a solution for these problems [4].

In other optoelectronic devices the ALD films find most often use in passivation and encapsulation. Silicon based solar cells is a good example of the former [5] and OLED displays from the latter application area [6].

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Applied Surface Science Division
Room 204 - Session AS-TuA

The Impact of Modeling (Ion, Electron) and Data Analysis on Applied Surface Science, a Celebration of the Career of Barbara Garrison

Moderators: Gregory L. Fisher, Physical Electronics, Alexander Shard, National Physical Laboratory, UK

2:20pm **AS-TuA1 Collective Action, the Key to Soft Molecule Desorption under Particle Bombardment***, **Arnaud Delcorte,*** Université catholique de Louvain, Belgium **INVITED**

The focus of this contribution is on desorption of large non-volatile organic molecules induced by ion beams, for 2D and 3D analysis by secondary ion mass spectrometry (SIMS). It is also the story of my long-term collaboration with Pr. Barbara Garrison since 1999, when I started my post-doc under her guidance. Our first molecular dynamics (MD) simulations of polystyrene emission from silver induced by atomic projectiles gave us direction: in order to emit large molecules with minimal internal energy, collective action of the substrate atoms was required, which only occurred in so-called high (sputter) yield events where most of the projectile energy was deposited in the extreme surface [1]. These high yield events, rare with atomic ions, happened to be the rule with cluster projectiles such as C_{60}, where the collision cascades fully overlapped [2]. The use of C_{60} therefore led to remarkable sputtering yield enhancements for organic samples, and much improved emission of molecular ions in SIMS [3]. Clusters were the solution. We then naturally moved to larger clusters, where the physics shifted again, to macroscopic-like impacts phenomena [4]. Our simulations using large organic and argon clusters showed similar trends and, in particular, they quantitatively predicted the experimental 'universal' sputtering curves for the Ar cluster bombardment of organics [5]. The simulations also uncovered a region of energy, scaled by the number of atoms in the projectile (E/n), where fragmentation was minimized and intact molecular emission, maximized. All of this could not have been achieved without the great collective spirit and action that were maintained by Pr. Garrison in her 'extended team' over the years.

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3:00pm **AS-TuA3 Mechanisms of the Generation of Nanoparticles and Surface Modification in Short Pulse Laser Ablation of Metal Targets in Liquids***, **Leonid Zhigilei**, C.-Y. Shih, M. Shugaev,* University of Virginia

The ability of short pulse laser ablation in liquids to produce clean colloidal nanoparticles and unusual surface morphology has been employed in a broad range of practical applications. In this presentation, the results of large-scale molecular dynamics simulations aimed at revealing the key processes that control the surface morphology and nanoparticle size distributions generated by pulsed laser ablation in liquids [1-4]. The simulations of Ag and Cr targets irradiated in water are performed with an advanced computational model combining a coarse-grained representation of liquid environment and an atomistic description of laser interaction with metal targets. One of the interesting predictions of simulations performed at sufficiently high laser fluences, in the regime of phase explosion, is the emergence of Rayleigh–Taylor and Richtmyer–Meshkov hydrodynamic instabilities at the interface between ablation plume and superheated water, leading to the formation of nanojets and emission of large droplets into the water environment. The droplets are rapidly quenched and solidified into nanoparticles featuring complex microstructure and metastable phases, as demonstrated by example structures shown in the middle of the cover. Rapid nucleation and growth of small nanoparticles in the silver–water mixing region and the breakup of the hot metal layer into larger droplets due to the hydrodynamic instabilities represent two distinct mechanisms of the nanoparticle formation that yield nanoparticles of two different size ranges as early as several nanoseconds after the laser irradiation. This computational prediction provides a plausible explanation for experimental observations of bimodal nanoparticle size distributions in short pulse laser ablation experiments.

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3:20pm **AS-TuA4 First Principles Thermodynamics and Molecular Modeling of Surfaces in Aqueous Environments***, **Donald Brenner**, Z. Rak, L. Su, J. Krim,* North Carolina State University

We have been using first-principles thermodynamics and molecular modeling to characterize the structure, stability and dynamics of solid surfaces in aqueous environments. This talk will focus on two recent examples from our research. The first involves understanding and predicting the thermodynamics of the corrosion of stainless steel and nickel alloys in contact with the coolant in nuclear pressurized water reactors, as well as the driving force that leads to unwanted deposits on the fuel rod cladding from the corrosion products. The second example is a molecular modeling study of the adhesion of functionalized nano-diamond clusters to a gold substrate. Our simulations have revealed a new phenomenon, a molecular water layer containing solvated counter ions between a gold substrate and a negative nano-diamond that is facilitated by surface functionalization, and that is not present for a positively charged nano-diamond. The resulting electro-static screening leads to a weaker adhesion of negative nano-diamonds compared to positive nano-diamonds, an effect that has been observed in prior experiments but not understood.

This work was supported by the Consortium for Advanced Simulation of Light-Water Reactors, a DoE Energy Hub, and by the National Science Foundation through grant DMR-1535082.

4:20pm **AS-TuA7 Computer Modeling of Cluster Projectile Impacts for SIMS Applications***, **Zbigniew Postawa**,* Jagiellonian University, Krakow, Poland **INVITED**

A few years ago, Secondary Ion Mass Spectrometry (SIMS) has celebrated its centennial. The first observation of secondary ions is credited to J.J. Thompson at the beginning of the twentieth century [1]. However, the golden era of SIMS began in the fifties and continues to this day. This period is associated with a plethora of ground-breaking equipment developments, experimental observations and theoretical explanations. Initially, theoretical descriptions were based on analytical models. However, soon it has been realized that a proper description of phenomena taking place in more complex materials goes beyond the capability of this treatment. The appearance of computers and computer simulations have breathed new life into the field [2]. Today, computer simulations are a vital counterpart to the experimental measurements due to the atomic resolution and ability to visualize processes taking place inside investigated solids. As ion beams have developed from argon, through gallium, gold, bismuth to metal clusters, C_{60} and now giant atomic and molecular clusters and as computers have become ever more powerful, analysis and simulation of ever more realistic materials has gone forward hand in hand. Barbara Garrison has been always at the forefront of all these endeavors.

In this talk, a few examples of theoretical studies, which Barbara has guided and/or inspired, will be given. Examples include efforts to understand a difference in processes stimulated by impacts of atomic and cluster projectiles [3], evolution of surface roughness during cluster bombardment and its influence on the depth resolution in depth profiling [4], and processes of molecular emission from cluster-bombarded novel ultra-thin graphene-based substrates used recently to enhance molecular ionization [5].

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5:00pm **AS-TuA9 Use of Ion-Solid Interactions Modeling and Theory for Real Applications in FIB Milling***, **Lucille Giannuzzi**,* L.A. Giannuzzi & Associates LLC

Many FIB techniques in sample preparation and prototyping have been developed with a knowledge and use of ion-solid interactions modeling and theory. Understanding ion-solid interactions at different incident angle, ion energy, dose, and effect of target crystallography, are crucial for quality FIB milling of materials [1,2]. A discussion on the modeling and theory of ion-solid interactions and its direct influence on FIB milling quality and results will be presented.

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5:20pm **AS-TuA10 The Influence of the Projectile Cluster on the Molecular Ionization Probability in SIMS***, **Lars Breuer**, A. Wucher,* Universität Duisburg-Essen, Germany*; N. Winograd,* The Pennsylvania State University

The implementation of cluster ion sources in secondary ion mass spectrometry (SIMS) opened the field to molecular imaging and depth profiling of organic materials. In the last years the trend to larger projectiles continued and led to gas cluster ion beams (GCIB) with projectiles consisting of thousands of atoms. The use of these projectiles not only reduces the chemical damage produced by the projectile impact and therefor preserves the molecular information, but also significantly increases the sputter yield of organic material. For the measured signal in a ToF-SIMS experiment the secondary ion yield is of greater interest. Here describes the probability that an intact quasi-molecular ion of species *i* is formed during the sputtering process. As for inorganics especially metals a long list of values for ionization probabilities has been reported in the literature only very little is known about ionization probabilities of organic molecules in particular under GCIB bombardment.

The knowledge of ionization probabilities and sputter yields is of great general importance. Not only is the process of ion formation not fully understood yet, but also can manipulating the ionization probability increase the sensitivity of the experiment. Possible approaches for such manipulations are changes is projectile size, kinetic energy and chemistry. The important question here is: “How much headroom is left to produce more secondary ions?”

To answer this question a measurement of the ion fraction in the flux of sputtered material is necessary. Such a measurement requires the direct comparison of the sputtered intact secondary (quasi-) molecular ion and its neutral counterparts. To perform such a measurement post-ionization without severe photo-fragmentation has to be performed. In our measurements we used a strong-field post-ionization scheme due to its universality and low fragmentation. In the past our lab performed this kind of measurements on material sputtered under C_{60} bombardment [1,2] which has been extended to the bombardment with GCIB in this study. As a result, we will compare ionization probabilities of sputtered molecular species under GCIB and C_{60} bombardment.

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5:40pm **AS-TuA11 In Situ Liquid SIMS, a Molecular Eye for Examination of Liquids and Liquid Interfaces***, **Zihua Zhu**[1], Y. Zhang,* Pacific Northwest National Laboratory **INVITED**

Secondary ion mass spectrometry (SIMS) has proven to be a powerful surface analysis tool, because it can provide elemental, isotopic and molecular information with excellent sensitivity and decent spatial resolution. However, SIMS is a high vacuum technique, and it normally is used to analyze solid samples. In recent years, in situ liquid SIMS was developed in my lab with collaboration with Dr. Xiao-Ying Yu, allowing molecular examination of various liquids and liquid interfaces. In brief, an interesting liquid can be sealed within a vacuum compatible device, and a thin silicon nitride (SiN) membrane is used to separate the liquid from vacuum. Then, we use a focused primary ion beam to drill an aperture through the SiN membrane to expose the liquid for SIMS examination. The key design of this idea is the diameter of the aperture: if the diameter is less than 2-3 microns, surface tension of the liquid can hold the liquid without any spraying out. Also, the evaporation from the aperture is controllable, making SIMS measurements fully feasible. If using a cluster primary ion beam, molecular signals from liquid surfaces and solid-liquid interfaces can be readily collected. In situ liquid SIMS has been used to investigate electrode-electrolyte interfaces during electrochemical or electro-catalytic reactions. The uniqueness of this novel approach is simultaneous collection of molecular evolution information of electrode surfaces, reactants, intermediates, and products under operando conditions, offering the possibility to elucidate complicated chemistries occurring at electrode-electrolyte interfaces (e.g., solid-electrolyte interphase in lithium ion batteries). More interestingly, the ionization process of in situ liquid SIMS may be softer than regular electrospray ionization, which is surprisingly different from the traditional opinion that SIMS ionization process is very hard with strong damage. This new finding will shed light on molecular investigation of ion solvation, nucleation before nanoparticle formation, and similar complex processes occurring in liquid environments.

Biomaterial Interfaces Division
Room 101B - Session BI+AS+IPF+NS-TuA

IoT Session: Biofabrication, Bioanalytics, Biosensors and Diagnostics and Flash Networking Session

Moderators: Graham Leggett, University of Sheffield, UK, Tobias Weidner, Aarhus University, Denmark

2:20pm **BI+AS+IPF+NS-TuA1 Functionalization of Silica Materials *via* Click Reaction of Surface Silanol Groups with Vinyl Sulfones***, **Fang Cheng**, H. Wang, W. He, B. Sun, J. Qu,* Dalian University of Technology, China

Silica-based materials are widely used in the fields of catalysis, chromatography, biomaterials, biosensing and drug delivery due to their earth abundance and low cost. Success of these applications mostly relies on the functionalization of silica surfaces, among which covalent binding of organic molecules is preferred. Common strategies for the covalent functionalization of silica materials involve either silane treatments or Si-H reactions. Each has its share of limitations, with the former suffering from self-polymerization and multilayer modifications, and the latter being sensitive to moisture and oxygen. Herein, we proposed the ‘click’ reaction of silanol groups with vinyl sulfones, which enables a new and simple strategy for functionalization of silica materials. For the first time, the ‘click’ concept was extended to silanol groups that are abundant on the surface of silica materials, using compounds bearing vinyl sulfone groups. By simply immersing silica materials in vinyl sulfone solutions at 60℃, functionalization could be achieved in hours in the presence of catalysts. The chemical stability of vinyl sulfones and mild reaction conditions make this strategy advantageous than silane treatments and Si-H reactions. We demonstrated that silica materials with sizes ranging from microscale to macroscale could all be functionalized. Using compounds bearing multiple vinyl sulfone groups, silica materials can be further functionalized with varies of biomolecules due to the versatile reactivity of vinyl sulfone group towards thiol, amino and alcohols. Furthermore, the stability of resulting Si-O-C bond can be tuned by the properties of the vinyl sulfone compounds (e.g., hydrophobicity and surface density) as well as the environmental factors (e.g., solvents, pH and temperature). Increase in the hydrophobicity and functionalization density of the vinyl sulfone compounds could increase the stability of Si-O-C bonds. Contrast to the high stability in

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[1] **ASSD Peter Sherwood Award**

organic solvents, degradation of Si-O-C bond can be realized in aqueous solutions, which can be accelerated by addition of acid or base. This is rarely observed with bonds produced based of silane treatments and Si-H reactions. It could broaden the biomedical applications of functionalized silica, for example, to provide tailored release of drugs or proteins from silica surface.

2:40pm **BI+AS+IPF+NS-TuA2 Organosilica pH Nanosensors Applied to Realtime Metabolite Monitoring***, **Kye Robinson**,* Monash University, Australia*; K. Thurecht,* University of Queensland, Australia*; S. Corrie,* Monash University, Australia

Continuous monitoring of biomarkers in biological environments is a key challenge for the development of biosensors capable of providing real-time feedback[1]. These sensors promise to aid in the treatment of diseases with a highly dynamic nature however current technologies remain scarce[1]. Nanoparticle based “optodes” have emerged as sensitive and tuneable biosensors, using chromo/ionophores to generate analyte-specific changes in fluorescence spectra in a dynamic and reversible manner. Currently this type of sensor suffers from limitations including leaching of reagents from the nanoparticles over time, combined with poor colloidal stability and resistance to fouling in biological fluids.

An organosilica core-shell pH sensitive nanoparticle containing a mixture of covalently incorporated pH-sensitive (shell) and pH-insensitive (core) fluorescent dyes has been developed. This platform demonstrates good long term stability (80 days), fast response time (<100 ms) and resistance to fouling in biological conditions[2]. This presentation will describe the modification of these pH sensing particles towards the production of a lactate responsive particle for sensing through coupling with lactate dehydrogenase. Here we will present our latest results focussed on enzyme encapsulation in addition to modulation of shell parameters including thickness and degree of crosslinking in order to tune response kinetics for application in biological tissues.

[1] Corrie, S. R. et al., Analyst, **2015**, 140, 4350-4364

[2] Robinson, K. J. et al., ACS Sensors, **2018**

3:00pm **BI+AS+IPF+NS-TuA3 Impact of Different Receptor Binding Modes on Surface Morphology and Electrochemical Properties of PNA-based Sensing Platforms***, **Johannes Daniel Bartl**,* Walter Schottky Institut (WSI) and Physics Department, Technische Universität München, Germany*; P. Scarbolo,* Dipartimento Politecnico di Ingegneria e Architettura (DPIA), Università degli Studi di Udine, Italy*; S. Gremmo, G. Rziga, M. Stutzmann,* Walter Schottky Institut (WSI) and Physics Department, Technische Universität München, Germany*; M. Tornow,* Molecular Electronics Group and Department of Electrical and Computer Engineering, Technische Universität München, Germany*; L. Selmi,* Dipartimento di Ingegneria "Enzo Ferrari" (DIEF), Università di Modena e Reggio Emilia, Italy*; A. Cattani-Scholz,* Walter Schottky Institut (WSI) and Physics Department, Technische Universität München, Germany

Silicon-based field-effect devices have been widely studied for label-free DNA detection in recent years. These devices rely on the detection of changes in the electrical surface potential during the DNA recognition event and thus require a reliable and selective immobilization of charged biomolecules on the device surface [1]. The preparation of self-assembled monolayers of phosphonic acids (SAMPs) on metal oxide surfaces is an efficient approach to generate well-defined organic interfaces with a high density of receptor binding sites close to the sensing surface [2,3]. In this work, we report the functionalization and characterization of silicon/silicon nitride surfaces with different types of peptide nucleic acid (PNA), a synthetic analogue to DNA [4].

Differently modified PNA molecules are covalently immobilized on the underlying SAMPs either in a multidentate or monodentate fashion to investigate the effect of different binding modes on receptor density and morphology important for PNA-DNA hybridization. Multidentate immobilization of the bioreceptors *via* C_6-SH attachment groups at the *γ*-points along the PNA backbone provides a rigid, lying configuration on the device surface (PNA 1), whereas a monodentate immobilization by Cys-capped PNA molecules (PNA 2) results in more flexible and more accessible receptor binding sites. Our results indicate that the presented functionalization scheme can be successfully applied to produce morphologically and electrochemically different PNA bioreceptor binding sites on silicon/silicon nitride surfaces. Consequently, a well-chosen modification of the PNA backbone is a valid approach to influence the sensing properties of surface-immobilized PNA bioreceptors, which might provide an additional parameter to further tune and tailor the sensing capabilities of PNA-based biosensing devices.

[1] Ingebrandt S. and Offenhausser A., *Phys. Status Solidi A* **203** (2006), 3399–3411.

[2] Chaki N. K. and Vijayamohanan K., *Biosens. & Bioelectron*. **17** (2002), 112.

[3] Stutzmann M., Garrido J. A., Eickhoff M. and Brandt M. S., *Phys. Status Solidi A* **203** (2006), 3424–3437.

[4] Nielsen P. E. and Egholm M. (ed.), Peptide Nucleic Acids, Horizon Scientific Press (1999).

3:20pm **BI+AS+IPF+NS-TuA4 Biosensor for Detection of Gasotransmitter from Living Cells Employing Silver Nanorods Array***, **Shashank Gahlaut**, C. Sharan, J.P. Singh,* Indian Institute of Technology Delhi, India

The detection of endogenous gases including H_2S is of immense interest nowadays as it opens the way to predict some diseases as well as an early stage diagnosis. These three gasotransmitter (H_2S, NO and CO) gaseous molecules transfer the information and give the signal for mainly cardiovascular diseases Therefore, its detection has crucial importance in bio-medical science. Here, we demonstrate H_2S detection from living cells using silver nanorods arrays fabricated by glancing angle deposition method. Colorimetric and wettability properties of silver nanorods are being observed for the gaseous detection. We use the model organism *E.coli* to demonstrate the feasibility of the method for the determination of live and resistant strains of the bacteria. For the human cell, we have used Hela cell line for the same. For the simplicity and feasibility of the technique, Android based mobile app has been developed for the colorimetric detection. Data obtained in this study show the potency of the system to identify live/dead bacteria with or without antibiotic treatment and compared with the time-consuming standard plating method, it a simple and cost-effective method for the estimation of living and resistant microorganism. The performance of AgNRs as H_2S gas sensor is investigated by its sensing ability of 5 ppm of gas with an exposure time of only 30 s. It has potential application in the area of antimicrobial resistance and bio-medical healthcare.

4:40pm **BI+AS+IPF+NS-TuA8 Polyzwitterion-modified Nanoparticles for Selective Antibody Separation***, F. Cheng, C. Zhu, **Wei He**, B. Sun, J. Qu,* Dalian University of Technology, China

Antibody separation is a key biopharmaceutical process, which requires high specificity and efficiency in isolating the biomacromolecule from a complex biological fluid. Development of the separation adsorbent benefits diagnostics and therapeutics, such as point-of-care testing, treatment of cancer and autoimmune disease. In the process of antibody separation, Protein A chromatography is a commonly employed adsorbent, which could obtain antibody in high purity from serum or ascites. In the process-scale purification and therapeutic plasma exchange, safety issues, e.g. leakage and instability of the immobilized Protein A, and cross-contamination during regeneration, are overwhelmed in biopharmaceutics. An alternative approach to Protein A chromatography is using synthetic ligand, molecular weight of which is commonly less than 200 Da. The main advantages of synthetic ligand are well-controlled chemical structure, low cost, ease in clean-in-place, and repeatable regeneration capability in harsh conditions. However, it is a challenge to adsorb antibody in a highly selective manner from a complex biological fluid, which consists a variety of proteins with a broad range of concentrations.

Herein, we report a facile method to develop a quick separation adsorbent, which adsorbs antibody from a complex biological fluid with a high specificity. Two types of zwitterionic polymer-modified magnetic nanoparticles (NPs) are fabricated by conjugating pSBMA onto PEI-precoated NPs via either one-step method (1S NPs) or two-step method (2S NPs). For both methods, divinyl sulfone is used as linker molecule. Although 1S NPs were capable of resisting both IgG and BSA, 2S NPs exhibited specificity toward IgG adsorption in complex biological fluids, e.g. mixture of serums and IgG. The moderate interactions (Kd ~1.2 µM) between IgG and 2S NPs are three orders of magnitude lower than IgG binding with Protein A (Kd 10nM) . Through complementary characterizations and analyses, we rationalize that the surface developed herein with IgG specificity contains two key components: polyzwitterions with short chain length and sulfone groups with high density.

5:00pm **BI+AS+IPF+NS-TuA9 Orienting Proteins on Surfaces with Site-specific Bioorthgonal Ligations***, **Riley Bednar**, R.A. Mehl,* Department of Biochemistry and Biophysics, Oregon State University

The functionalization of material surfaces with proteins is of great importance to a number of technologies, from industrial processes to biomedical diagnostics. However, while it has been proposed that orientation may be important to the function of such biomaterials, efforts to study such roles are hampered by a lack of rapid, quantitative, and orientation-specific immobilization techniques which will reduce non-specific fouling, and allow substoichiometric attachment of proteins onto surfaces in an orientation-controlled manner. Here, Carbonic Anydrase II (HCA)—a 30 kDA, monomeric metalloenzyme which catalyzes the interconversion of carbon dioxide to bicarbonate—is immobilized onto strained *trans*-cyclooctene (sTCO)-functionalized magnetic resin in an orientation-specific manner via bioorthogonal ligation with a site-specifically installed tetrazine-containing amino acid (Tet2.0).

5:20pm **BI+AS+IPF+NS-TuA10 High-throughput Study of the Role of Spatial Organization on the Activity of Surface-Bound Enzymes***, **Nourin Alsharif,*** Boston University*; T. Lawton, J. Uzarski,* Natick Soldier Research, Development and Engineering Center*; K.A. Brown,* Boston University

Many of the exceptional properties of natural materials (e.g. fracture toughness of bones, strength to weight ratio of bamboo) can be attributed to their structural hierarchy, which originates, in part, from the nanoscale organization of the enzymes that synthesize these materials. In order to best utilize such enzymes *ex vivo* to grow engineered biomaterials, the role of this multiscale organization must be understood. Here, we report a novel strategy for studying the activity of arrangements of enzymes within a multifunctional material in a high throughput manner. In particular, we use top-down patterning techniques in conjunction with small molecule self-assembly to designate enzyme-binding regions amidst a non-binding, hydrophobic background. Key to this experimental scheme is the parallel nature of both the fabrication and the characterization processes that enable the efficient study of many geometric parameters of the enzyme-binding features. These parameters include, (1) feature size, (2) density of enzyme within each feature, and (3) distance between features. This level of control can in principle allow us to separate effects of reaction kinetics and substrate diffusion. Two strategies have been explored for the immobilization of enzymes including click chemistry to non-natural amino acids and binding to poly-histidine affinity tags. Top-down lithography and enzyme assembly were verified using a variety of surface characterization techniques including atomic force microscopy, X-ray photoelectron spectroscopy, infrared spectroscopy, spectroscopic ellipsometry, and contact angle goniometry. Initially, this high throughput paradigm is used to develop a fluorimetric assay to quantify the activity of surface-bound enzymes as a function of their spatial organization. Together with the widespread utilization of high throughput techniques in synthetic biology, the ability to study spatial organization in a rapid fashion is expected to dramatically improve *ex vivo* applications of enzymes.

5:40pm **BI+AS+IPF+NS-TuA11 Fabrication of Amino acid Contained Poly-lactic Acid Nanofibers by Electrospinning***, C. Li,* National Yang Ming University, Taiwan, Republic of China*; J.H. Hsieh,* Ming Chi University of Technology, Taiwan, Republic of China*; **P.H. Lin,*** National Yang Ming University, Taiwan, Republic of China

Polylactic acid (PLA, $[C_3H_4O_2]_n$, CAS 26161-42-2) is a biodegradable and thermoplastic polymer. PLA is naturally produced and can be extracted from many plants such as sugarcane, cornstarch or cassava roots. Typical industrial production processes for PLA are direct condensation of lactic acid monomers (~100°C - 160°C) and ring-opening polymerization of lactide with metal catalysts. For applications in bulk forms, PLA can be produced by extrusion, casting, injection molding and spin coating or even 3d printing.

In cell and tissue engineering applications, amino acids are essential ingredients for cell-tissue culture, implants/replacements, drugs and treatment tests. There are twenty amino acids appearing in human genetic codes by triplet codons and usually categorized according to their polarity, acidity/basicity.

In this study, we fabricate nanofibers by electrospinning on a spin-coated PLA film. This specially designed combination of PLA films and nanofibers is meant to have enduring interfacial adhesion between the two for biomedical applications such as implants. Both PLA nanofibers and films are mixed with selected amino acids. Five amino acids were chosen: tryptophan (Trp,), methionine (Met,), serine (Ser,), glutamate (Glu,) and arginine (Arg,). The selection is based on the different electrical polarity of each amino acid. The electrical polarity has profound effects on the solubility, pH acidity of amino acids in water and many other associated biochemical functions. These amino acids are representatives of certain biochemical features for potentially different influences in our applications for cell culture.

The electrospinning process is controlled by several parameters such as the voltage of power supply, feeding velocity of polymer solution through the syringe pump, electrical field strength and distance to the collection plate of nanofibers. Different combinations of these parameters are studied to determine an optimal control for fiber formation. Properties of and microstructures of deposited films and nanofibers are investigated as following: thickness and deposition rate by surface profilometer; microstructures by Fourier transform infrared spectrometer (FTIR); surface morphology by scanning electron microscope (SEM); optical properties by UV-Visible-IR spectrometer and wettability by the contact angle.

Processing and Characterization of Air-Liquid, Solid-Liquid and Air-Solid Interfaces Focus Topic
Room 202A - Session PC+AS+BI+EM+NS+PB+SS-TuA

Progress in Industrial Processes and Characterization of Interfaces and Gas-Solid Interfacial Processes and Characterization

Moderators: Jeffrey Fenton, Medtronic, Xiao-Ying Yu, Pacific Northwest National Laboratory

2:20pm **PC+AS+BI+EM+NS+PB+SS-TuA1 Near Ambient Pressure XPS as a Standard Tool for True Non-destructive High-throughput Surface Chemical Analysis in Industrial Applications***, **Andreas Thissen,** P. Dietrich,* SPECS Surface Nano Analysis GmbH, Germany*; M. Kjaervik, W.E.S. Unger,* Bundesanstalt für Materialforschung und -prüfung (BAM), Germany **INVITED**

Since many decades X-ray excited Photoelectron Spectroscopy (XPS) or Electron Spectroscopy for Chemical Analysis (ESCA) is a well-accepted standard method for non-destructive chemical analysis of solid surfaces. Over the last years it has been possible to develop XPS instrumentation, that can work far beyond the standard conditions of high or ultrahigh vacuum: Near Ambient Pressure (NAP)-XPS, or ESCA under environmental conditions has become a method, that enters the field of standard surface chemical analysis and thus also the industrial sector. The main reason for this is the extremely fast solid surface analysis of any (degassing or non-degassing) material. Furthermore the environmental conditions around the sample avoid strong surface degradation due to vacuum or photon stimulated desorption. Even during the analysis the sample stays under its equilibrium conditions. Last, but not least the surrounding gas pressures of a couple of mbar acts as built-in charge neutralization on any type of material. This Environmental Charge Compensation (ECC) also decreases the negative influences of the characterization on the sample constitution. All this considered, NAP-XPS is capable of true non-destructive high throughput analysis of sample surfaces. The influence of the ambient conditions on quantification in XPS will be demonstrated and discussed.

After a short summary of the relevant development steps in NAP-XPS instrumentation over the last forty years, this presentation summarizes results of surface chemical analysis on insulating polymer samples, showing the spectroscopic resolution for C1s, F1s and O1s emission lines as a comparison for PET and PTFE. Using this, the application of ECC to bulk insulators (polymeric materials, ceramics), food samples, pharmaceuticals, and different biological materials is demonstrated. The unique ability to measure liquids, like water or aqueous solutions allow for studies of drying processes of liquid containing materials, like paper or absorber materials and finally also opens the field to medical applications, especially to studies of drug uptake into gram-negative bacteria embedded in biofilms.

The last part summarizes methods to analyze materials and device under working conditions. As examples reduction and reoxidation of catalytically active compounds and operando electrochemistry will be presented. An outlook to future industrial applications will be given.

ACKNOWLEDGEMENTS: 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.

3:00pm **PC+AS+BI+EM+NS+PB+SS-TuA3 Surface Modifications in the Medical Device Field – Understanding of Methods to Control Adhesion and Reactions That Materials Undergo***, **Jeffrey Fenton,** B. Theilacker, A. Belu, B. Tischendorf,* Medtronic **INVITED**

Advances in materials chemistry have increased the need for deep understanding of process-material interactions and their role in device or component longevity. In the medical device industry advances are due in part to operating in a federally regulated environment where it may be necessary to understand not only what is the surface chemistry, but how various chemistries interact with the body, what is clean, or where does a foreign material originate. This presentation will highlight case studies where microscopy and surface characterization techniques were successfully applied to help further understand materials performance and interactions with the body.

Polymers used in the medical industry often undergo numerous clinical trials, laboratory testing, and development to understand the body and polymer interactions. The interactions these materials often undergo may potentially be at odds with the bulk material properties. For example, it may be desirable to modify surface properties of PTFE for polymer adhesion or modify a surface chemistry to improve bio compatibility. Methods of polymer surface modification will be presented that either enable or hinder the adhesion of a material to the surface.

Lithium ions generated during battery discharge may undergo interactions with components in or near the battery forming chemistries that may degrade battery performance or material stability. For example, lithium ions are known to interact with silica containing glass to form lithium silicide. The formation of these silicides can degrade the hermetic seal of feedthroughs. One method of studying these interactions is in-situ interfacial reactions characterization. This facile method of generating ions in-situ can be leveraged to understand what reactions may occur at a substrate surface.

The application of surface characterization techniques such as X-ray photoelectron spectroscopy (XPS), Time of Flight-Secondary Ion Mass Spectrometry (TOF-SIMS), and Scanning Electron Microscopy (SEM) provide unique insights into surface modifications and can help ensure the reliability of medical devices. These techniques support the development and manufacturing of Medtronic products such as packing and perfusion devices to improve processing conditions, understand failure modes, and surface-tissue interactions.

4:20pm **PC+AS+BI+EM+NS+PB+SS-TuA7 Ambient Pressure X-Ray Photoelectron Spectroscopy Studies of Catalytically Active Interfaces using Electron Transparent Graphene Membranes***, R. Mom, L. Frevel,* Fritz-Haber Institute of the Max Planck Society, Germany*; J.J. Velasco-Velez,* MPI CEC Mülheim, Germany*; T.E. Jones, M. Plodinec,* Fritz-Haber Institute of the Max Planck Society, Germany*; R. Schlögl,* MPI CEC Mülheim, Germany*;* ***Axel Knop-Gericke****,* Fritz Haber Institute of the Max Planck Society, Germany **INVITED**

Green production of hydrogen will be an important building block in the transition to a carbon-balanced economy and could be realized by electrolytic water splitting powered by cheap renewable energy sources. Water electrolysis is currently limited by the oxygen evolution reaction (OER) and development of the associated catalysts is proceeding slowly, mainly due to missing descriptors for activity and stability of working OER catalysts. Herein, we contribute to that emerging field with in situ XPS and NEXAFS on iridium anodes. In our in situ cell the catalyst is probed through a graphene layer, which traps an electrolyte layer around the catalyst and provides electrical contact for separated iridium nanoparticles. In this way we enhance spectroscopic signal from the active surface relative to the bulk of the catalyst and reduce mass transport problems. In taking advantage of these benefits, we found that the two well-known oxidation waves occurring before the OER onset are connected to the development of two different types of electron deficient oxygen species, which are bound to one (μ_1) or two (μ_2) iridium atoms. It appears that oxygen is not only a “non-innocent ligand”, but rather a protagonist in the catalysis of the OER.

During the electrochemical reduction of oxygen, platinum catalysts are often (partially) oxidized. While these platinum oxides are thought to play a crucial role in fuel cell degradation, their nature remains unclear. We studied the electrochemical oxidation of Pt nanoparticles using in situ XPS. By sandwiching the particles between a graphene sheet and a proton exchange membrane that is wetted from the rear, a confined electrolyte layer was formed, allowing us to probe the catalyst under wet electrochemical conditions. We show that the behavior at the onset of Pt oxidation is influenced by the choice of proton exchange membrane, yet universally involves PtO_2 formation. The oxidation process is fast: even bulk oxide growth occurs on the sub-minute timescale. Thus, our observations indicate that PtO_2 may take part in the transient processes that dominate Pt electrode degradation.

5:00pm **PC+AS+BI+EM+NS+PB+SS-TuA9 The Influence of Density and Chemical Bonding on Atomic and Molecular Structures of Alcohols, Water and Oxides***,* ***Gabor A. Somorjai****,* University of California at Berkeley **INVITED**

Alcohol oxidation reaction over platinum nanoparticles with size ranging from 2 to 8 nm deposited on mesoporous silica MCF-17 was studied in the gas and liquid phases. Among methanol, ethanol, 2-propanol, and 2-butanol oxidations, the turnover frequency increased as the nanoparticle size became large in both reaction phases. The activation energy in the gas phase was higher than that in the liquid phase. Water co-adsorption decreased the turnover rate of all the gas and liquid phase oxidations except for the gas-phase 2-butanol case, while certain amount of water promoted 2-propanol oxidation in the liquid phase. Sum frequency generation vibrational spectroscopy (SFG) study and DFT calculation revealed that the alcohol molecules pack horizontally on the metal surface in low concentration and stand up in high concentration, which affects the dissociation of b-hydrogen of the alcohol as the critical step in alcohol oxidation.

Ice surfaces have water layers with thickness ranging from one monolayer at 100K to 30 layers of 273K. At the interfaces of two ice cubes, ice layers grow at the disappearing water interfaces (regelation). SFG studies of water surfaces show three peaks in the vibrational spectrum; “free OH^-”, liquid like hydrogen bonded water, with half bilayer termination, and ice-like water, with bilayer termination, with more hydrogen bonds.

Most nanocatalysts are composed of highly dispersed transition metal nanoparticles on oxides. The interface between the metal nanoparticles and the oxides plays a crucial role in determining the catalytic performance of nanocatalysts. Due to non-adiabatic electronic excitation, energetic electrons in metals can be generated during exothermic chemical processes. The energy barrier formed at the metal-oxide interfaces leads to the irreversible transport of energetic, or hot, electrons. The dopants and impurities present on the oxides can generate additional charge carriers or oxygen vacancies that affect the catalytic activity. The accumulations or depletion of hot electrons on the metal nanoparticles, in turn, can also influence the catalytic reactions. In this talk, we outline recent studies of the role of metal oxide interfaces and characteristics of fast charge transfer between metals and oxides that lead to ionization of molecules at the interface. The molecular ions produce so-called acid-base reactions. The electronic configuration of metal-oxide nanocatalysts during catalytic reactions will be introduced and its influence on heterogeneous catalysis will be outlined.

5:40pm **PC+AS+BI+EM+NS+PB+SS-TuA11 Atomic Scale Observation of Oxidation and Reduction of Palladium Surface***,* ***Takehiro Tamaoka****, H. Yoshida, S. Takeda,* Osaka University, Japan

Reaction processes on metal surfaces under gas environment have been investigated in various research fields such as catalysis, gas sensing, and many more. Palladium is a well–known material which is used for hydrogen storage, hydrogen sensing, and exhaust catalysis. Therefore, the phase transition of palladium in hydrogen or oxygen has been extensively investigated by means of environmental transmission electron microscopy (ETEM). However, the oxidation and reduction process of palladium surface at the atomic scale remain poorly understood.

Here, we investigated the surface structure of a wedge–shaped palladium specimen in both hydrogen and oxygen by means of in-situ atomic resolution ETEM. Under ambient condition the surface of palladium is oxidized by several nanometers. After introducing hydrogen (100 Pa) in ETEM, the native oxide layer (PdO) was reduced to metallic fcc palladium even at room temperature. After exposure and exhaustion of hydrogen, we introduced oxygen (100 Pa) in ETEM. The palladium oxide was reproduced and the ETEM results show that the oxidation started from step edges and terraces and proceeded until the palladium surface was completely covered by the palladium oxide.

We also show that oxidation of palladium is dependent on the history of hydrogen exposure. When the duration of hydrogen exposure was over 90 min., we found that the surface was not oxidized. This was not due to bulk hydrogenation as demonstrated by our electron energy loss spectroscopy (EELS) results. We performed similar studies for the surface of platinum in oxygen after prolonged hydrogen exposure. However in platinum, the oxidation of the surface was not suppressed. This suggests that the process for suppression of oxidation, after prolonged hydrogen exposure, exists for palladium and not for platinum.

From these results, we hypothesize possible processes that explain how the prolonged hydrogen exposure suppresses the oxidation of palladium surface. We will also present atomic-scale in-situ movies on the surface dynamics in palladium and platinum in various processing.

6:00pm **PC+AS+BI+EM+NS+PB+SS-TuA12 Polymorphism of Hydrogen-Bonded Clusters at the Vacuum-Solid Interface***, **Angela Silski**, J. Petersen,* University of Notre Dame*; R.D. Brown,* Clarkson University*; S. Corcelli, S.A. Kandel,* University of Notre Dame

Molecular self-assembly is an attractive bottom-up approach to nanostructure fabrication. Using molecules as building blocks and carefully tuning the non-covalent intermolecular interactions, unique nanostructured architectures can be designed. Given the structure/function relationship on the nano- and meso-scale, this bottom-up approach to designing new architectures is critical in the careful design of novel materials with desired chemical properties. In this study, the role of hydrogen bond donor/acceptor position in metastable cluster formation is explored using scanning tunneling microscopy (STM) with complementary density functional theory (DFT) calculations. We observe a metastable cyclic pentamer for isatin (1H-indole-2,3-dione) with DFT providing support for a cyclic structure stabilized by both NH...O and CH...O hydrogen bonds between neighboring molecules. The CH...O hydrogen bond is made between the 7-position proton acting as the hydrogen bond donor and the 3-position carbonyl as the hydrogen bond acceptor, and calculations indicate that the isatin pentamer structure is 12 kJ/mol more stable than the dimer on the per molecule basis. To probe the importance of the CH...O hydrogen bond in stabilizing the isatin pentamer, we compare to isatin derivatives: we replace the 3-position carbonyl with a methyl group (3-methyl 2-oxindole), the 7-position proton with a fluorine (7-fluoroisatin), systematically move the location of the hydrogen bond donor/acceptor by one position, (phthalimide), and remove of the primary hydrogen bond donor (1,2-indandione and 1,3-indandione). We show that cyclic pentamer formation is either altered or precluded as a result of these substitutions. Additionally, the importance of CH...O bonding in forming isatin pentamers is supported by electrospray ionization mass spectrometry (ESI-MS) measurements, which include a magic-number isatin pentamer peak, whereas the derivative molecules show little clustering under the same conditions. This work is significant in understanding the role that the position of the hydrogen bond donor/acceptor groups has on the resulting 2D supramolecular assemblies.

Processing and Characterization of Air-Liquid, Solid-Liquid and Air-Solid Interfaces Focus Topic
Room Hall B - Session PC+AS+BI+EM+NS+PB+SS-TuP

Processing and Characterization of Gas-Liquid, Solid-Liquid, and Gas-Solid Interfaces

PC+AS+BI+EM+NS+PB+SS-TuP1 Operando Photoelectron Spectroscopic Study of Copper-based Oxide Semiconductor Interface with Water*, **Pitambar Sapkota**, S. Ptasinska,* University of Notre Dame*; A. Cabrera,* Instituto de Física, Pontificia Universidad Católica de Chile

The quest for suitable semiconductor photoelectrodes to build efficient and stable photoelectrochemical (PEC) cells for solar water splitting is continually growing in the material sciences and solar energy community. Along with good stability in aqueous media, such photoelectrodes should have suitable band-edges and band-gap energies properly matching both the water oxidation-reduction potential and the solar spectrum, respectively. Copper-based oxide semiconductors are promising candidates fulfilling these criteria, but little is known about the interfacial properties of these compounds with H_2O under operational conditions. Therefore, knowledge of their surface dynamics and interfacial reactions under realistic conditions is essential to improve our understanding of water-splitting mechanism, as well as to increase the stability and efficacy of PEC devices. Ambient pressure X-ray photoelectron spectroscopy was used to characterize the semiconductor surface and study the chemical reactions occurring at the interface under the reaction conditions. In this study, thin films of $CuFeO_2$ and $CuFe_{1-x}Ga_xO_2$ composites were exposed to various H_2O pressures and temperatures. Water interactions with the Cu-based oxide surface and the electronic structures of the surface atoms were evaluated from the Cu 2p, Fe 2p, C 1s and O 1s photoemission spectra to identify surface species newly formed.

PC+AS+BI+EM+NS+PB+SS-TuP2 Interfacial Water in Silicon-based Catalytic Motors*, **Jordi Fraxedas**, K. Zhang, B. Sepulveda, M.J. Esplandiu,* Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Spain*; X. Garcia, J. Llorca,* Institute of Energy Technologies, Department of Chemical Engineering and Barcelona Research Center in Multiscale Science and Engineering. Universitat Politècnica de Catalunya, Spain*; V. Perez-Dieste, C. Escudero,* Alba Synchrotron Light Source, Spain

Self-propelled motors that can harvest chemical energy from their surroundings to convert it in mechanical energy are at the cutting edge of nanotechnology for their appealing applications in e.g., environmental remediation and nanobiomedicine. A full understanding of the propulsion mechanism is crucial to improve their performance and controllability. Recently, a simple motor made of silicon and a noble metal that can operate with visible light has been developed [1]. The photoactivation mechanism and consequent motion is essentially based on the formation of electron/hole pairs. The holes are strong oxidizing agents for the species in the fluid producing protons and the electrons can diffuse towards the metal surface and participate in the counterpart reduction reaction. As a result, a gradient of proton concentration is formed in the fluid which builds-up an electric field driving the motion of the fluid through electro-osmosis. A mechanism that competes with the electro-osmotic process is based on diffusion-osmosis and is triggered by the redox decomposition exclusively at the metal surface and is not light responsive. We have recently shown that it is possible to enhance/suppress one mechanism over the other by tuning the surface roughness of the micromotor metal. Thus, the actuation mechanism can be switched from light-controlled electrokinetics to light-insensitive diffusio-osmosis by only increasing the metal surface roughness [2].

We have recently performed near ambient pressure photoemission studies of Pt/Si micromotor surfaces activated by oxygen plasma in water atmosphere at the NAPP endstation of the CIRCE beamline at the ALBA synchrotron near Barcelona. We have used p-type silicon substrates with one half covered with a Pt film with a thickness of about 50 nm grown by both e-beam and sputtering deposition. The results reveal a chemical gradient at the Si/Pt edge with a reduction of the Pt species. The analysis has to carefully consider the photochemical reactions induced by the combined action of the impinging beam and the water condensed at the surfaces. The beam induced damage evolves in two regimes: an initial preferential reduction of Pt4+ species and then the reduction of Pt2+ species, which increases the metallic character of the surface.

[1] M.J. Esplandiu, A. Afshar Farniya, A. Bachtold, ACS Nano, 9, 11234 (2015).

[2] K. Zhang, J. Fraxedas, B. Sepulveda, M. J. Esplandiu, ACS Appl. Mater. Interfaces 9, 44948 (2017).

PC+AS+BI+EM+NS+PB+SS-TuP3 Chiral Modification of Oxide-Supported Pt Surfaces: An in-situ ATR-IR Study*, **Yufei Ni**,* University of California, Riverside*; F. Zaera,* University of California, Riverside

The synthesis of enantiopure compounds is of great significance to the designing of pharmaceuticals and agro products. Possible methods for the manufacture of enantiopure chemicals include the separation of racemic product mixtures and reactions with other chiral chemicals, but perhaps the most promising procedure is the use of enantioselective heterogeneous catalysis. Chiral modification of catalytically active metals such as Pt and Ni is believed to be the most feasible approach to produce chiral heterogeneous catalysts. In this context, the use of cinchona alkaloids-modified Pt for the hydrogenation of activated ketones has drawn particular attention in the past few decades. A better understanding of how these chiral modifiers work to bestow enantioselectivity is still a prerequisite for the design of such catalysts.

In this project, we have used attenuated total reflection infrared absorption spectroscopy (ATR-IR) to investigate the details of the adsorption of such cinchona-alkaloid chiral modifiers on the Pt surfaces of supported catalysts in situ at the liquid-solid interface. It was determined that adsorption can be only observed after H_2 pretreatment of the catalyst. A comparison study in terms of adsorption strength was carried out using not only cinchona alkaloids such as cinchonidine and cinchonine but also simpler alternatives such as (R)- or (S)-(−)-1-(1-naphthyl) ethylamine (NEA), naphthylmethyl amine, and dimethyl naphthyl ethylamine.The adsorption strength of the different modifier molecules was found to be quite different among those compounds. This is illustrated by the fact that quinoline can displace s-NEA from Pt but not vice versa, for instance, and by the observation that when Pt is exposed to a solution containing both quinoline and s-NEA only the quinoline's signature peaks can be detected by ATR-IR spectroscopy. The ordering of the modifiers studied in terms of adsorption strength was found to correlate with their ability to chirally modify the Pt catalyst during the hydrogenation of unsaturated aldehydes.

Finally, it was found that NEA bonds to the metal through the nitrogen atom of its anime moiety, and not through the aromatic ring as commonly believed.

PC+AS+BI+EM+NS+PB+SS-TuP4 Wettability Behaviour of Synthesized Carbon Nanospheres and its Application as a Photocatalyst*, **Sonal Singhal**, A.K. Shukla,* IIT Delhi, India

Superhydrophobic and superhydrophilic surfaces have been widely investigated due to their diverse range of applications such as self-cleaning, microfluidic application in biotechnology, corrosion, Anti-reflecting coatings and microelectronic mechanical system etc. Here, a facile chemical vapour deposition method is reported for the synthesis of carbon nanospheres (CNSs). Henceforth, the morphology of as-synthesized sample is characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). X-ray diffraction (XRD), Raman spectroscopy and FTIR spectroscopy are used to determine the phase purity, chemical composition and presence of chemical bonds on the surface of synthesized CNSs. TEM and SEM results reveal the presence of CNSs with a diameter ranging from 50 nm to 400 nm. Raman spectroscopy confirms the presence of disordered carbon and low graphitization, which are also confirmed by TEM and XRD results. Optical properties of as-synthesized CNSs is investigated by UV-Vis spectroscopy and photoluminescence. Wettability behaviour of as-synthesized carbon nanospheres is investigated by contact angle measurements. CNSs shows a water contact angle of 152^0, which confirms the fabrication of superhydrophobic carbon nanosphere surface. After the proper explanation of wettability behaviour, it also discusses the application of as-synthesized CNSs as a photocatalyst. As it is well known, catalyst enhances the chemical reaction rate without changing its properties. Therefore, various kind of catalysts has been developed for the purpose to enhance the catalysis for environmental applications. Among different materials, carbon-based materials are widely used as a catalyst support due to their excellent properties. Considering these facts, the degradation of an organic pollutant under UV light is discussed here using CNSs.

PC+AS+BI+EM+NS+PB+SS-TuP5 Thermally Driven Solid-solid Li$^+$ Transfer into Nanostructured TiO$_2$, ***Tiffany Kaspar***, *T. Varga,* Pacific Northwest National Laboratory; *D.A. Shapiro,* Advanced Light Source, Lawrence Berkeley National Laboratory; *A. Martinez, Y. Shin, K.S. Han, M.-S. Lee, S. Thevuthasan, V. Murugesan,* Pacific Northwest National Laboratory

Due to their good chemical stability, strong oxidation capability, and desirable lithium electrochemical activity, nanostructured titanium dioxide (TiO_2) anode materials have received considerable attention recently. Decreasing the particle size to 10-20 nm can increase the electrochemical capacity to 200-300 $mAhg^{-1}$. Furthermore, nanostructured TiO_2 anodes are non-toxic and would be suitable for cost effective mass production. Among the rutile, anatase, and brookite polymorphs of TiO_2, anatase nanoparticles have shown the best Li ion insertion properties and maximum reduction, indicating increased Li ion intercalation into the material. Here, we have synthesized 10-20 nm anatase TiO_2 nanoparticles and contacted them with solid Li- bis(trifluoromethanesulfonyl)imide (LiTFSI) as a function of temperature to understand the chemical and structural effects associated with thermally driven solid-solid Li^+ transfer to, and intercalation in, TiO_2 nanoparticles. We have used a combination of x-ray photoelectron spectroscopy (XPS), Ti L-edge scanning transmission x-ray microscopy (STXM), Raman spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy to gain a fundamental understanding of the structural evolution of TiO_2 nanoparticles during Li^+ intercalation. Our results indicate that thermally driven solid-solid Li^+ transfer to TiO_2 has occurred, and altered the TiO_2 structure at the edges of the agglomerated nanoparticles.

Applied Surface Science Division
Room 204 - Session AS+NS+SA-WeM
Beyond Traditional Surface Analysis

Moderators: Mark Engelhard, Pacific Northwest National Laboratory, Kathryn Lloyd, DuPont Corporate Center for Analytical Sciences

8:00am **AS+NS+SA-WeM1 Solar Wind Interaction with Carbonate Deposits on Asteroid (1) Ceres' Surface: The Role of Surface Analysis in Laboratory Planetary Science***, **Catherine Dukes**, G. Rodriguez Lopez, C. Bu,* University of Virginia

Bright deposits of anhydrous carbonates across the dark background of dwarf-planet Ceres have been identified by Dawn's VIR spectrometer with a composition that varies from natrite with minor amounts of ammonium bicarbonate within the Cerealia and Vinalia Faculae to magnesite, calcite, and dolomite in other high-albedo regions [1]. These deposits are expected to derive from the aqueous alteration of volatile-containing silicates, forming a viscous brine below Ceres' solid crust. Hydrated salts from this reservoir are deposited on the planetary surface by extrusion through vents or co-ejected by jets of sub-surface water ice. Water loss in the material occurs with exposure to the low pressure environment on Ceres' surface as a function of exposure time, even at temperatures < 240 K [2].

Unprotected from the impacts of solar particles, cosmic rays, and meteorites, anhydrous salts undergo chemical and physical change (space weathering), which can be remotely identified by optical reflectance. The effect of solar-wind ions on carbonates can be simulated in the laboratory, and the correlation between surface composition and morphology with optical change can be used to infer physical processes occurring on airless planetary bodies. We investigate the stability of carbonates and measure systematic darkening with 4 keV He-ion fluence, a potential geologic chronometer for Ceres' bright deposits.

Carbonate powders are pressed into pellets, then introduced into vacuum (10^{-9} Torr) and cooled to ~110/200 K.

An external-beam from an FT-IR is used to perform *in-vacuo* reflectance measurement. Spectra were acquired at varied fluence, equivalent to solar irradiation of ~300 - 30,000 years at 2.8 A.U. Changes in surface composition and molecular chemistry were investigated by *in-situ* X-ray photoelectron spectroscopy (XPS).

Blueish luminescence of sodium carbonates with He^+ is observed. Vis-NIR darkening (~80%) of natrite (Na_2CO_3)occurs after 10^{18} He cm^{-2}, with reddening of the visible spectral slope. Similar darkening is noted for 1.3 - 5 µm, along with attenuation of carbonate overtones. Concomitant XPS measurement shows a reduction of carbon and oxygen, with enhancement of sodium. Exposure of the darkened sample to 10,000 L H_2O-vapor results in brightening to > 80%.

Ion-induced darkening of Ceres' natrite deposits is expected to occur on a time-scale of 100 - 1000 years, and can be reversed by exposure to water vapor. For deposits of varied albedo, this suggests that the brightest areas are the most recent deposits or the most recently exposed to water.

[1] DeSantis et al. (2016) Nature 536, 54-57

[2] Bu et al. (2017) Icarus doi.org/10.1016/j.icarus.2017.12.036

8:20am **AS+NS+SA-WeM2 Looking Deeper and Smaller: Enhancing XPS by Hard X-ray Probes and High-resolution Imaging***, **Olivier Renault**,* CEA/LETI-University Grenoble Alpes, France*; C. Zborowski,* University of Southern Denmark*; J.-P. Rueff,* Synchrotron SOLEIL, L'orme des Merisiers, France*; Y. Yamashita, S. Ueda,* NIMS, Japan*; G.A. Grenet,* Lyon Institute of Nanotechnology, France*; S. Tougaard,* University of Southern Denmark

X-ray photoelectron spectroscopy (XPS) has become a mature technique with a widespread use spanning from fundamental research to R&D labs. In parallel, the intrinsic complexity of materials and systems to be analyzed by XPS has increased. Some of the limitation of XPS are of concern if a non-destructive, non-invasive analytical protocol is the key issue. These are, especially, the poor lateral resolution and the poor bulk sensitivity, making impossible the analysis of microscopic features and buried interfaces in a reliable way.

In this contribution, we review the capabilities of current and novel techniques to get into: (i) high lateral resolution and quantitative micro-analysis using spectroscopic imaging implemented by X-ray PhotoElectron Emission Microscopy (XPEEM); (ii) high depth sensitivity offered by Hard X-ray Photoelectron Spectroscopy (HAXPES), coupled or not with inelastic background analysis to futher enhance information depth up to nearly 100 nm.

We will highlight the capabilities of each techniques by different practical examples in the field of 2D materials [1] and device technology [2, 3], emphasizing particularly the perspectives offered by novel laboratory hard X-ray sources [4].

[1] H. Kim, O. Renault et al., Physical Review B, 2016. 94(8): p. 081401.

[2] P. Risterucci, O. Renault et al., Applied Surface Science, 2017, 402: p. 78-85.

[3] C. Zborowski, et al., Applied Surface Science, 2018. 432(Part A): p. 60-70.

[4] O. Renault, E. Martinez, et al., Surf. Interface Anal. 2018 (in press).

8:40am **AS+NS+SA-WeM3 Reenvisioning Amphiphilicity: Translating Cell Membrane Design Principles to Synthetic 2D Materials***, **Shelley Claridge**,* Purdue University **INVITED**

2D materials such as graphene exhibit unique electronic and mechanical properties that promise substantial advantages in applications ranging from nanoelectronics to human health. Such interfaces are often functionalized noncovalently with lying-down phases of functional molecules to avoid disrupting electronic structure within the basal plane. Interfacial structures have commonly been characterized down to sub-nm scales using scanning probe techniques such as STM, either in vacuum, or at a solid-liquid interface with a nonpolar liquid (e.g. octadecene). However, molecules used in this approach are often structurally similar to amphiphiles such as fatty acids and phospholipids found in biological cell membranes, suggesting possible utility in *aqueous* environments. At the same time, the overall surface chemistry is strikingly different than that of the cell membrane -- in essence, the surface chemistry is that of a repeating cross-section of a lipid bilayer, with both hydrophilic and hydrophobic components exposed, forming a striped amphiphilic structure with sub-10-nm periodicity.

As 2D materials are integrated into hybrid materials and devices, this noncovalent amphiphilic interfacial structure raises two classes of significant questions requiring interfacial analysis: ***(1) How do noncovalent lying-down ligand layers respond to solution or thermal processing?*** What are the best ways to probe controlled *disordering* across scales from nm to mm at an interface with a polar liquid? If ligand dynamics vary with structure, to what extent can design principles from the cell membrane be invoked to control chemical functionality and reactions at the interface? ***(2) Can noncovalently-adsorbed layers be patterned to template further interactions with the environment?*** Lying-down phases of phospholipids and fatty acids present 1-nm-wide stripes of ordered chemical functional groups, suggesting the possibility of controlling processes such as crystallization, phase segregation, or analyte binding. We examine these questions, again developing approaches to characterize interface structure across the range of relevant length scales, and invoking structural design principles from the cell membrane.

9:20am **AS+NS+SA-WeM5 Microstructural Effects on Surface Potential of Amorphous Solid Water***, **Caixia Bu**, C.A. Dukes,* University of Virginia

Amorphous solid water (ASW) formed by vapor deposition on substrates <~130 K is of interest for its abundance in Earth's upper atmosphere, icy planetary bodies, and throughout the interstellar medium, as well as its use as model material in many disciplines. Two crucial characteristics of ASW are a self-induced negative surface potential and formation of nanopores [1]. Here, we examine the role of microstructure, including nanopores, on the spontaneous surface potential of ASW, and describe the complementary experimental techniques used, which have application for other microporous solids.

ASW films were deposited by directed vapor beams onto a He-cooled quartz-crystal microbalance (QCM) under ultra-high vacuum. The integrated pore volume (porosity) was calculated by combining the areal mass measured via QCM and thickness measured by UV-visible interferometry. The integrated surface area was indicative by the abundance of incompletely coordinated surface water molecules (H_2O) on the pores, using the O-H dangling bonds (DBs) measured by FT-IR spectroscopy. An *in-situ* Kelvin probe measured film surface potential. A long-distance optical microscope monitored film morphology *in vacuo*. Annealing effects were investigated by heating the film at 1.8 K/min.

The magnitude of the negative surface potential ($|V_s|$) increased linearly with film thickness at rates ($|\Delta V_s/\Delta L|$) that decreased with increasing growth temperature (T_g = 10–110 K), keeping deposition angle at $\theta = 0°$

(angle between vapor beam and QCM normal); at T_g = 30 K, the $|\Delta V_s/\Delta L|$ decreased with increasing θ (= 10−75°). ASW porosity showed no dependence on T_g at θ = 0°, but increased significantly with increasing θ. The H_2O DBs decreased/increased with increasing T_g/θ, showing similar trends as the $|\Delta V_s/\Delta L|$. Upon heating, the most striking result was that the DB at ~3720 cm^{-1} (from two-coordinated H_2O) and the $|V_s|$ had similar temperature-dependent evolutions. By correlating all measurements, we propose that the observed intrinsic ASW surface potential results from aligned incompletely-coordinated H_2O on the pore surfaces [2].

The $|V_s|$ decreased abruptly when ASW thickness exceeded a critical value (L_c), and cracks appeared in the optical images of the films. The L_c, ~1−5 μm (T_g = 10–50 K; θ = 0–55°), increased with T_g and θ, suggesting dependences on the microporous structure. We explain such dependences of L_c in the context of Griffith theory and estimate the tensile strength of ASW to be ~25–40 MPa [3].

We acknowledge support from the NASA LASER Program.

[1]Raut et al., *J. Chem. Phys.***127**, 204713 (2007); [2]Bu et al., *J. Chem. Phys.***143**, 074702 (2015); [3]Bu et al., *Appl. Phys. Lett.***109**, 201902 (2016).

9:40am **AS+NS+SA-WeM6 Speciation and Reactivity of Organic Matter in Uranium Mine Wastes from Laguna- New Mexico: An Application of Surface Sciences in Environmental Systems.**, ***Carmen A. Velasco,*** *A.M. Ali,* University of New Mexico*; C. Osburn,* North Carolina State University*; K. Artyushkova, J.M. Cerrato,* University of New Mexico

The co-occurrence of organic matter and uranium in the Jackpile Morrison formation, New Mexico was investigated using spectroscopy, microscopy, and water chemistry techniques to better understand the effects of organic matter on uranium (U) binding from abandoned U mine wastes. Samples were collected from the Jackpile Mine (JP)- New Mexico. The mean concentration of acid extractable content for mine waste from the JP was 2.61±0.09% U. Results from microprobe mapping suggest that U particles are surrounded by carbon (C) inclusions, while results from XRF analyses showed 2.78% (JP) carbon (C). Loss on ignition (LOI) analysis showed that 19.90±0.95% of organic carbon within the samples. Thermal gravimetric analysis (TGA) show the maximum weight loss between 105°C and 505°C, confirming that change on mass after the LOI is likely due to the loss of organic content of the samples. Analyses using XPS suggest that changes occur on the C binding and U oxidation state after modifying the pH in batch experiments. Emission Matrix (EMM) identified humic-acid and fulvic-acid like components present in the organic matter comprised in the mine waste, which is consistent with the organic functional groups detected by XPS. These findings suggest that uranium minerals are possibly complexed carboxylic functional groups from humic-and fulvic like substances. This study identified the relevance of considering the binding of U and C in mine wastes to better understand U mobilization in the environment.

*This work was awarded the best talk award at the 2018 NMAVS Symposium (Albuquerque-May2018)

11:00am **AS+NS+SA-WeM10 Optical Constants Measured for Iridium and Samarium by Reflection Electron Energy-loss Spectroscopy Spectra**, ***LiHao Yang,*** *H. Xu,* University of Science and Technology of China*; A. Sulyok, M. Menyhard,* Institute for Technical Physics and Materials Science Centre for Energy Research, Hungarian Academy of Sciences (MTA)*; K. Tokesi,* Institute for Nuclear Research, Hungarian Academy of Sciences (ATOMKI)*; Z.J. Ding,* University of Science and Technology of China

The optical properties, as one of the most important physical properties of materials, arouse a continuous interest of researchers. Accurate measurement of optical data by optical methods in a photon energy range up to 100 eV is still insufficient as special experimental conditions are required during the measurements in vacuum ultraviolet region (20-50 eV). In recent years a well-established technique based on the reflection electron energy loss spectroscopy (REELS) has been developed to obtain optical constants in a rather wide range of electron energy loss. The REELS method does not require a complicated process for preparation of samples and the incident electron energy is usually around a few keV. However, the REELS spectrum usually contains not only bulk excitation but also surface excitation. To remove the surface excitation effect from the REELS spectrum in data analysis, Da et al. [1] have developed a reverse Monte Carlo (RMC) method for the derivation of the energy loss function (ELF) which is directly related to optical constants of a solid.

In the present work, reflection electron energy loss spectra of Ir and Sm were measured at several primary energies ranging from 0.5 keV up to 2 keV and in a wide energy-loss range. Polycrystalline Ir and Sm samples were cleaned by Ar+ ion bombardment. To minimize the surface roughening and damage, glancing incidence angle of 80° with respect the surface normal and low projectile energy of 1 keV were applied with the rotated sample during the sputtering. Cleanliness of surface was checked by continuous detection of main Auger peaks of C and O. A reverse Monte Carlo simulation was performed to extract ELFs of these metals from experimental REELS spectra. All the ELFs have produced REELS spectra in a good agreement within the experimental uncertainty. The reliability of the obtained optical data has been confirmed by applying the Thomas-Ritchie-Kuhn (f-sum rule) and the perfect-screening sum rules (p-sum rule). The good agreement indicates that RMC treats accurately the surface excitation effect which is well removed from the final ELF. Comparisons of our data with other sources from experimental measurements are given.

The work was support by the National Natural Science Foundation of China (No. 11574289) and Special Program for Applied Research on Super Computation of the NSFC-Guangdong Joint Fund (2nd phase) under Grant No. U1501501.

Reference:

[1] B. Da, Y. Sun, S. F. Mao, Z. M. Zhang, H. Jin, H. Yoshikawa, S. Tanuma, and Z. J. Ding, J. Appl. Phys. 113, 214303 (2013).

11:20am **AS+NS+SA-WeM11 X-Ray Photoelectron Spectroscopy and Electrical Modeling of Electrowetting on Dielectric Devices**, ***Pinar Aydogan Gokturk,*** Bikent University, Turkey*; B. Ulgut, S. Suzer,* Bilkent University, Turkey

Electrowetting on dielectrics (EWOD) is a process of changing the contact angle of a droplet sitting on the dielectric covered electrode by the application of external electric field. In majority of the electrowetting experiments reported in the literature, water or aqueous salt solutions are used and ambient medium is either the air, or another immiscible liquid like oil. In this study, for the first time two non-aqueous liquids; (i) polyethylene glycol with an average molecular weight of 600 Da, and (ii) DEME-TFSI ionic liquid, both with low vapor pressure and volatility, are used as droplets in the UHV chamber of an x-ray photoelectron spectrometer (XPS) with traditional electrowetting on dielectric device geometry. With the experimental determination on tracing the electrical potential developments on and around the droplet, using the shifts in the binding energy positions of peaks coming from the liquid and/or the substrate, under imposed AC and DC electrical fields, we are aiming to shed light on the numerous models employed for simulating the electrowetting phenomenon. Additionally, using XPS and incorporating real capacitors and resistors, we mimic and check on the commonly used models used for simulating the electrical behavior of the EWOD systems. Possible and accepted electrical circuit models are also used to simulate the XPS data.

11:40am **AS+NS+SA-WeM12 Near Ambient Pressure XPS Study of Oxygen Binding to the Surface of Transition Metal-nitrogen-carbon Electrocatalysts for Oxygen Reduction***, K. Artyushkova,* ***Yechuan Chen,*** *P. Atanassov,* University of New Mexico

The most promising class of platinum group metal-free materials for oxygen reduction reaction (ORR) is based on graphene-like carbon containing nitrogen and transition metal (MNC). 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.

The mechanism of oxygen reduction reaction in metal-nitrogen-carbon (MNC) catalysts has been studied by a combination of spectroscopic and theoretical structure-to-activity studies. Using inhibitors that have unique spectral signatures and have strong binding to the active sites allows elucidating the relationship between the chemistry of active sites and its activity.

We will report laboratory-based and near ambient pressure (NAP-XPS) analysis for series of electrocatalysts belonging to Fe-N-carbon families. X-ray photoelectron spectroscopic analysis of the interaction of complexing agents based on phosphonate and *in situ* monitoring of oxygen binding to metal-free active sites provides an important insight into the reaction mechanism. The effect the nitrogen chemistry and the type of iron on the oxygen binding was investigated by NAPXPS under an oxygen environment at operating temperature of the fuel cell. Preferential oxygen binding to different types of nitrogen and iron moieties in presence and absence of inhibitor was followed by spectroscopic changes in high-resolution nitrogen photopeak.

12:00pm **AS+NS+SA-WeM13 Surface Chemistry of Scandium***, **Michael Brumbach**, D.A. Casalnuovo, E.V. Barnat, C. Winters, D. Robinson Brown, C.S. Snow, A.M. Grillet,* Sandia National Laboratories

Manipulation of metal surface chemistry through vacuum gas dosing has been demonstrated for many years. Additionally, ex situ preparation methods, ion sputtering, and/or in vacuo thermal treatment are all known to change surface properties through oxidation, removal of oxide, change in microstructure, altering contaminants, or other mechanisms. While these studies have been performed for decades, there are few examples of these experiments for pure scandium films. Furthermore, few examples of dosing clean scandium surfaces under vacuum have been published. In this work, scandium films were treated with UV/ozone ex situ cleaning, ion sputtering, and thermal treatment under UHV. These surfaces were then exposed to different gases in the millitorr pressure range for extended periods of time. An optical emission spectrometer was used to monitor the composition of the dosing gas. Surfaces were analyzed before and after dosing. In concert with the gas analyses, the changes in surface chemistry of scandium could be correlated to the dosing species. This work discusses the X-ray photoelectron peak fitting of scandium and the changes in chemistry that can be observed through surface exposures.

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Industrial Physics Forum
Room 101B - Session IPF+AS+BI+NS-WeM

IoT Session: Bioanalytics, Biosensors and Diagnostics

Moderators: Anna Belu, Medtronic, Sally McArthur, Swinburne University of Technology and CSIRO

8:40am **IPF+AS+BI+NS-WeM3 Harnessing Bacteria for Fabrication of Photoelectrodes and Pressure Sensors***, Y. Feng, K.E. Marusak, Y. Cao, E. Ngaboyamahina, J. Glass, L. You, **Stefan Zauscher**,* Duke University **INVITED**

Conventional methods for material fabrication often require harsh reaction conditions, have low energy efficiency, and can cause a negative impact on the environment and human health. In contrast, structured materials with well-defined physical and chemical properties emerge spontaneously in diverse biological systems. However, these natural processes are not readily programmable. By taking a synthetic-biology approach, we demonstrate a method for the fabrication of semiconducting, transition metal nanoparticles (NPs) with tunable bandgap and useful photoelectric properties, through bacterial precipitation. Surface analytic measurements revealed that our bacterially precipitated CdS NPs are agglomerates of quantum dots (QDs) in a carbon-rich matrix. We discovered that the precipitation conditions of the bacteria can be tuned to produce NPs with bandgaps that range from quantum-confined to bulk CdS. We determined the photoelectrochemical properties and energy band structure of thin films prepared from these NPs by electrochemical measurements. By taking advantage of the organic matrix, which is residual from the biosynthesis process, we fabricated a prototype photo-charged capacitor electrode by incorporating the bacterially precipitated CdS with a reduced graphene oxide sheet. Furthermore, we show the programmable, three-dimensional (3D) material fabrication using pattern-forming bacteria growing on top of permeable membranes as the structural scaffold. When the bacteria are equipped with an engineered protein that enables the assembly of gold (Au) nanoparticles into a hybrid organic-inorganic dome structure, the resulting hybrid structure functions as a pressure sensor that responds to touch. We furthermore show that the response dynamics are determined by the geometry of the structure, which is programmable by the membrane properties and the extent of circuit activation. By taking advantage of this property, we demonstrate signal sensing and processing using one or multiple bacterially assembled structures. Our work provides the first demonstration of using engineered cells to generate functional hybrid materials with programmable electronic properties and architectures for energy conversion, energy storage, and for signal sensing and transduction.

9:20am **IPF+AS+BI+NS-WeM5 Surface Chemistry and Surface Analysis: Their Importance and Application in Industrial Genomics***, **Fiona Black**,* Illumina Inc. **INVITED**

Understanding the genome has the power to revolutionize health. However, building robust and scalable tools to interrogate single base variants with high robustness requires a system level approach to integrate surface patterning and activation, biosensing, and imaging. This talk will review how micro-patterning, bioanalytical controls, surface analytical techniques and measurement tools are applied in an industrial setting to develop and manufacture cutting edge systems for sequencing and genotyping applications

11:00am **IPF+AS+BI+NS-WeM10 Design and Evaluation of Organosilica Nanosensors for Continuous Molecular Monitoring in Complex Biological Environments***, **Simon Corrie**,* Monash Univ., Melbourne AU **INVITED**

Continuous monitoring of biomarkers in biological environments is a key challenge for the development of biosensors capable of providing real-time feedback. Sensors capable of continuous pH monitoring have already found applications in detection of bacterial infections and have potential for aiding in treatment of dynamic diseases. Nanoparticle based "optodes" have emerged as sensitive and tuneable biosensors, using chromo/ionophores to generate analyte-specific changes in fluorescence spectra in a dynamic and reversible manner. Current key limitations of these materials include leaching of reagents from the nanoparticles over time, combined with poor colloidal stability in biological fluids.

Organosilica is a promising material for developing stable biosensors, allowing simple control over size, interfacial chemistry and porosity. This presentation will describe the development of a core-shell nanoparticle containing a mixture of covalently incorporated pH-sensitive (shell) and pH-insensitive (core) fluorescent dyes. Attachment of anti-fouling polymers is used reduce aggregation and biofouling in biological media. Fluorescence analysis of the nanoparticles reveals that the shell/core fluorescence ratio is highly sensitive to pH over a physiological range with the response time <1s. The sensitivity and dynamic range can be tuned by varying material properties of the shell (primarily thickness and porosity). We will present our latest results on the application of these nanosensors for continuous, real-time monitoring, including in bacterial cultures, subcutaneous mouse "tattoos," and in 3D hydrogel scaffolds.

11:40am **IPF+AS+BI+NS-WeM12 Optoregulated Biointerfaces***, **Aránzazu del Campo**,* INM-Leibniz Institute for New Materials, Germany **INVITED**

Cells interact with their microenvironment by engaging membrane receptors with complementary partners at the surrounding matrix or at other neighbouring cells. These receptor complexes, often associated to cytoskeletal structures, allow exchange of biochemical and mechanical information. The ability to quantify this exchange is crucial for our understanding of cellular behavioru and responses to external factors. Using model biointerfaces with optoregulated interaction possibilities, selective membrane receptors in living cells can be addressed in situ, i.e. on a sensor surface, while quantifying specific cellular responses. Light-regulated tools to apply and sense cell biochemical and mechanical interactions will be presented.

Processing and Characterization of Air-Liquid, Solid-Liquid and Air-Solid Interfaces Focus Topic
Room 202A - Session PC+AS+BI+EM+PB+SS-WeM

Novel Approaches and Challenges of Interfaces

Moderators: Andrei Kolmakov, National Institute of Standards and Technology (NIST), Xiao-Ying Yu, Pacific Northwest National Laboratory

8:00am **PC+AS+BI+EM+PB+SS-WeM1 Probing Chemical Species and Potential Profiles of Electrified Interfaces***, **Ethan J. Crumlin**,* Advanced Light Source, Lawrence Berkeley National Laboratory **INVITED**

Interfaces play an important role in nearly all aspects of life, and are essential for electrochemistry. Electrochemical systems ranging from high temperature solid oxide fuel cells (SOFC) to batteries to capacitors have a wide range of important interfaces between solids, liquids, and gases which play a pivotal role in how energy is stored, transferred, and/or converted. This talk will focus on our use of ambient pressure XPS (APXPS) to directly probe the solid/liquid electrochemical interface. In particular, I will discuss how we were able to probe the potential drop within the electrochemical double layer (EDL) as well as the potential of zero charge under polarization conditions. This unique approach was accomplished by measuring spectral changes observed in both the electrolyte (water) and a neutral spectator probing molecule (pyrazine). By combining these experiments with numerical simulations provided the ability to discern the shape of the electrochemical double layer profile as a function of both electrolyte concentration and applied potentials. Extending beyond the EDL, I will highlight some of our recent investigations into both the oxygen evolution reaction on a platinum electrode as well as a magnesium electrode in a non-aqueous electrolyte. Information gained from these studies will aid in the guided design and control of future electrochemical interfaces.

8:40am **PC+AS+BI+EM+PB+SS-WeM3 Observation of Electron Transfer in Riboflavin Reduction by In Situ Liquid SIMS***, **Rachel Komorek**, X.F. Yu, Z.H. Zhu, X-Y. Yu,* Pacific Northwest National Laboratory

Riboflavin is of vital significance in living processes as a precursor of the two important coenzymes flavin mononucleotide (FMN) and flavin adenine dinucleotide (FAD).[1] The isoalloxazine ring in riboflavin plays an important role in energy supplementation and cellular respiration, since it has the capability to accept electrons in some redox reactions.[2] Understanding riboflavin reduction could potentially bring insight into the electron transfer process between cell surfaces and conductive materials. Thus, the electrochemical reduction process of riboflavin has drawn increasing attention. In this study, the riboflavin reduction mechanism in an aqueous solution has been investigated using time-of-flight secondary ion mass spectrometry (ToF-SIMS) with the electrochemical cell.[3, 4] Positive and negative ion mode mass spectra were used to depict the molecular information of species dissolved in the electrolyte. The distribution of key reduction intermediates were mapped at the electrode-electrolyte interface using dynamic depth profiling. To examine product formation as a function of applied potentials, measurements were made by holding the potential at 0, -0.3, 0.3, and 0.6 V respectively, once interesting electrochemistry was determined using the cyclic voltammogram. Furthermore, gold and graphite electrodes were both used in our experiment to investigate if the electrode surface plays a role in in the electrochemical reaction mechanism. Preliminary spectral principal component analysis (PCA) results have shown key chemical distinctions in the electrolyte at 0, -0.3, 0.3, and 0.6 V. Selected peak spectral PCA is required to gain a better understanding of this observation, which will allow for a more comprehensive chemical profile of the electron transfer process in riboflavin redox reactions.

Key words: in situ liquid SIMS, SALVI, riboflavin reduction, electrochemistry, electron transfer

References

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3. B Liu, et al., In situ chemical probing of the electrode–electrolyte interface by ToF-SIMS. *Lab Chip* (2014), **14**, 855-9.

4. J Yu et al., Capturing the transient species at the electrode-electrolyte interface by *in situ* dynamic molecular imaging. *Chem. Comm*. (2016), **73**, 10929-11206.

9:00am **PC+AS+BI+EM+PB+SS-WeM4 Electrowetting of Liquid Drops Revisited by XPS***, **Sefik Suzer**, P. Gokturk, B. Ulgut,* Bilkent University, Turkey

Electrowetting behavior of liquid drops has been followed in-situ and in-vacuum using XPS in a chemically resolved fashion, under both dc and ac excitations. Various Liquid drops, compatible with the UHV conditions, consisted of an Ionic Liquid (DEME-TFSI), Poly-ethylene-glycol (M.W. ~600 amu) and their mixtures. For the dielectric substrate, a ~300 nm thick silicon oxide (SiO_2/Si) without and with a thin hydrophobic coating (CYTOP) has been employed. XPS data have been recorded both in the conventional scan- and also in the fast (<1s) snap-shot modes. Intensity and position of the peaks, representing the liquid drops (F1s in the case of the IL, or C1s/O1s of the PEG) as well as those of the substrates (Si2p for the oxide only and F1s for the hydrophobic coated one) have been recorded under various electrical excitations. Under ac excitation at a fixed frequency, intensity modulations in the XPS peaks reveal geometrical changes of the drops, while the peak position modulations reveal electrical potentials developed. Monitoring position modulations as a function of the changes in the ac frequency (10^{-2} – 10^5 Hz) allows us to tap into ionic, dipolar and electrical contributions of the dielectric susceptibility of both the liquid drops and the substrates. Experimental details and various application will be presented and discussed.

*This work is partially supported by TUBITAK through Grant No. 215Z534

9:20am **PC+AS+BI+EM+PB+SS-WeM5 Probing Interfaces in Heterogeneous Catalysts at Atomic Scale: Current and Emerging STEM Techniques***, M. Chi, **Wenpei Gao**,* Oak Ridge National Laboratory **INVITED**

Chemical reactions take place on the surfaces and interfaces of heterogeneous catalyst systems. Depending on the phase of the reactant, the reactive interfaces include those between solid-gas, solid-liquid, and triple-phase interfaces of solid-gas-liquid. At these interfaces, the catalyst provides active sites where the reactants are adsorbed, activated, and converted to new chemical species that are eventually released from the catalyst surface. The ability of catalysts in promoting these reactions is determined by the surface binding energy, which can be modified by tuning the interfacial atomic arrangements or by forming new interfaces, e.g., forming core-shell structures. Understanding the formation of these interfaces during synthesis and their structural and chemical evolution during operation are important to the rational design of future high-performance catalysts. Probing these dynamically evolving interfaces at a sufficient spatial resolution, however, presents many challenging. Recent work on elucidating the formation and the operation mechanisms of interfaces in precious metal-based heterogeneous catalysts using *in situ* atomic-scale scanning transmission electron microscopy (STEM) techniques will be discussed. Several emerging STEM-based methods, such as vibration spectroscopy and atomic-scale differential phase contrast imaging that are currently under development within the microscopy community will be introduced, and their prospective influence on future studies to design functional interfaces in heterogeneous catalysts will be discussed.

Acknowledgements: Research supported by the Center for Nanophase Materials Sciences, which is a U.S. Department of Energy (DOE) Office of Science User Facility.

11:00am **PC+AS+BI+EM+PB+SS-WeM10 From 2D to Advanced 3D Surface Functionalization using Self-limiting Reactions in the Fluidized Bed Reactor Technology***, **Didier Arl**, T. Da Cunha, N. Adjeroud, K. Menguelti, M. Gerard, D. Lenoble,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

The integration of novel functional nanomaterials like high specific surface powders in polymeric or inorganic matrices requires a fine control of their properties. The design of these nanoscopic agents is linked to the development of nanotechnology processes which can be transferred from planar substrates to complex 3D surfaces. In this framework we showed how self-limiting reactions inspired by Atomic Layer Deposition can be applied to functionalize powder by using a specifically designed Fluidized Bed Reactor. A specific interest has been given to work in non-saturated regime with nickel or Cobalt acetylacetonate to obtain well controlled metal nanocatalysts of 5-10nm diameter. Depending on the process window, some interesting properties have been demonstrated such as ferromagnetic behavior or the systematic recover of the Metal-Carbide phase that increase the throughput of Carbon Nanotubes growth. These activated nanostructures can expressly improve the electrical, the thermal or the mechanical properties of some related composites depending on how some processing parameters such as exposure time, pressure or local temperature can be tailored.

Plasma Science and Technology Division
Room 104B - Session PS+AS+EL+EM+SE-WeM

Current and Future Stars of the AVS Symposium I

Moderator: Eric A. Joseph, IBM Research Division, T.J. Watson Research Center

8:20am **PS+AS+EL+EM+SE-WeM2 Invited Talk-Future Stars of AVS Session: Ellipsometry at THz Frequencies: New Approaches for Metrology and Metamaterial-based Sensing***, **Tino Hofmann**[1],* University of North Carolina at Charlotte

Spectroscopic ellipsometry at terahertz frequencies has seen substantial advancements over the last several years. Now, instruments are available which allow precise measurements of the material's complex dielectric function including its anisotropy. This access to accurate electromagnetic

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[1] **Future Stars of the AVS**

material properties at THz frequencies is essential for the development of increasingly advanced THz optical systems and a prerequisite for the design and manufacturing of optical elements for this spectral range.

In this talk I will give an overview of recent developments in the implementation of THz ellipsometry and focus on applications where THz ellipsometry contributed valuable material parameters. In combination with external magnetic fields generalized THz ellipsometry allows the accurate measurement of the optical Hall effect. The optical Hall effect enables the precise determination of the free charge carrier properties effective mass, mobility, and density in semiconductor heterostructures at THz frequencies without the need of electrical contacts and will be discussed in detail.

The exploration of novel physical phenomena observed in artificially structured metamaterials and the application thereof is of interest due to its relevance for the design and fabrication of novel THz optical elements and sensors. Metamaterials have attracted continued interest for almost two decades due to their unique electromagnetic properties, which can differ substantially from their constituents and often do not even exist in naturally occurring materials. We have demonstrated that although being orders of magnitude smaller than the probing wavelength, metamaterials composed of highly-ordered 3-dimensional metal nanostructures exhibit a strong anisotropic optical response at THz frequencies. I will discuss how these interesting optical properties may be used for novel THz sensor and device designs.

8:40am **PS+AS+EL+EM+SE-WeM3 Invited Talk-Future Stars of AVS Session: Remote Epitaxy – The Future for Stackable SiC Electronics***, Rachael Myers-Ward*[1]*,* U.S. Naval Research Laboratory*; J. Kim,* Massachusetts Institute of Technology*; M.T. DeJarld,* US Naval Research Laboratory*; K. Qiao, Y. Kim,* Massachusetts Institute of Technology*; S.P. Pavunny, D.K. Gaskill,* U.S. Naval Research Laboratory

Ideally, electronic heterostructures from dissimilar materials leads to enhanced functionality. Yet, experimentally forming these heterostructures is challenging due to lattice or thermal coefficient of expansion mismatch leading to defect formation or thermally driven atomic diffusion resulting in cross-doping and gradual junction transitions. These challenges may be overcome with the discovery of remote epitaxy and 2D layer transfer [1]. Here, SiC epitaxy is performed on epitaxial graphene as the electrostatic fields from the substrate penetrate the graphene and guide adatom registry. The film is easily peeled away since the graphene is not bonded to either the substrate or epilayer; the epilayer is then van der Waals bonded to a different material enabling new functionality. We will present experimental results on the remote epitaxy of SiC, illustrating potential quantum science applications.

There are three necessary steps to create remote epitaxy. The first is to grow epitaxial graphene on SiC, followed by transferring the graphene to a desired substrate (if different from SiC), and finally the growth of the remote epitaxial layer. If the remote epitaxy is to be SiC, which is the focus of this paper, the second step is not needed. Epitaxial graphene (EG) was first synthesized on 4H- and 6H-SiC in a horizontal hot-wall CVD reactor between 1540 and 1580 °C in 10 slm of Ar and 100 mbar [2]. The growth temperature was dependent upon the offcut of the substrate, where substrates with higher offcuts require a lower growth temperature to ensure 1 ML of EG, which is desired to assist in SiC adatom registry during growth. SiC remote epitaxy was then performed on the EG using silane (2% in H_2) and propane precursors, where the SiC polytype replicated the underlying substrate. In an effort to transfer the remote SiC epi/EG to another substrate such as SiO_2/Si, a metallization step was performed. Thin Ti and/or Ni layers were initially deposited followed by a thicker high stress metal to create strain and aide in removing the remote SiC epi/EG from the SiC substrate [1]. Once transferred, the metal was removed via a metal etch.

In this work, we will discuss the important parameters needed for successful remote SiC epitaxy, such as metallization, graphene thickness and remote epitaxy growth temperature. The epitaxial morphology characterized by SEM and Nomarski microscopy and graphene coverage and transfer evaluated by Raman spectroscopy will be presented.

[1] Kim, *et al*., Nature 544, 340 (2017).

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9:00am **PS+AS+EL+EM+SE-WeM4 Invited Talk-Future Stars of AVS Session: Low-Temperature Growth for 3D Integration of van der Waals Materials***, Christopher L. Hinkle*[2]*,* University of Texas at Dallas

The integration of novel logic and memory devices, fabricated from van der Waals materials, into CMOS process flows with a goal of improving system-level Energy-Delay-Product (EDP) for data abundant applications will be discussed. Focusing on materials growth and integration techniques that utilize non-equilibrium, kinetically restricted strategies, coupled with in-situ characterization, enables the realization of atomic configurations and materials that are challenging to make but once attained, display enhanced and unique properties. These strategies become necessary for most future technologies where thermal budgets are constrained and conformal growth over selective areas and 3-dimensional structures are required.

In this work, we demonstrate the high-quality MBE heterostructure growth of various layered materials by van der Waals epitaxy (VDWE). The coupling of different types of van der Waals materials including transition metal dichalcogenide thin films (e.g., WSe_2, WTe_2, $HfSe_2$), helical Te thin films, and topological insulators (e.g., $Bi_{2}Se_3$) allows for the fabrication of novel electronic devices that take advantage of unique quantum confinement and spin-based characteristics. We demonstrate how the van der Waals interactions allow for heteroepitaxy of significantly lattice-mismatched materials without strain or misfit dislocations. We will discuss TMDs, Te, and TIs grown on atomic layer deposited (ALD) high-k oxides on a Si platform as well as flexible substrates and demonstrate field-effect transistors with back-end-of-line (<450 °C) and even flexible plastics (<200 °C) compatible fabrication temperatures. High performance transistors with field-effect mobilities as high as 700 cm^2/V-s are demonstrated. The achievement of high-mobility transistor channels at low processing temperatures shows the potential for integrating van der Waals materials into new technologies.

This work was supported in part by the Center for Low Energy Systems Technology (LEAST), one of six centers supported by the STARnet phase of the Focus Center Research Program (FCRP), a Semiconductor Research Corporation program sponsored by MARCO and DARPA. This work is also supported in part by NEWLIMITS, a center in nCORE, a Semiconductor Research Corporation (SRC) program sponsored by NIST through award number 70NANB17H041.

9:20am **PS+AS+EL+EM+SE-WeM5 Invited Talk-Future Stars of AVS Session: Engineering the Properties at Heusler Interfaces***, Jason Kawasaki*[3]*,* University of Wisconsin - Madison

The Heusler compounds are a ripe platform for engineering and discovering emergent electronic, magnetic, topological, and ferroic properties at crystalline interfaces, either with other functional Heuslers or with compound semiconductor or oxide substrates. In these applications, the ability to control interfaces with near atomic level control is of tantamount importance; however, challenges such as interdiffusion have hampered their development. Here, I will discuss our efforts to control the properties of Heusler interfaces using precision growth by molecular beam epitaxy (MBE). Results will be presented in three areas: (1) the use of epitaxial strain to stabilize the hexagonal phase of several polar metal candidates, (2) the use of monolayer graphene diffusion barriers to enable high temperature growth and performance of spintronic devices, and (3) the phase segregation of ferromagnetic FeV nanostructures from a semiconducting FeVSb matrix with coherent epitaxial interfaces. Together, these examples illustrate the power of epitaxy and interfaces in controlling the properties of Heuslers and other intermetallic compounds, and integrating them onto commonly used semiconductor substrate platforms.

9:40am **PS+AS+EL+EM+SE-WeM6 Invited Talk-Future Star of AVS Session: Atom Probe Tomography for 3D Semiconductor Devices Applications***, Ajay Kumar Kambham*[4]*,* GLOBALFOUNDRIES U.S. Inc.

Device structures are rapidly scaling down to the nanometer regime with the ongoing development in semiconductor device technology. Along with this, it is ever critical need to engineer dopant profiles and to define the formation of junctions in Metal-oxide field effect transistors (MOSFETs). This is increasingly challenging considering the severity of short channel effects (SCEs). Indeed, one type of SCE in MOSFET devices known to cause performance degradation is Drain Induced Barrier Lowering (DIBL). To reduce DIBL, dopant junction profiles are made more abrupt. This can be done through the introduction of Sigma/cavity, fully depleted silicon-on-

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[1] **Future Stars of the AVS**

[2] **Future Stars of the AVS**

[3] **Future Stars of the AVS**

[4] **Future Stars of the AVS**

insulator (FDSOI) structures and the modulation of stress through optimal engineered epitaxial buffer layers. To assess the quality over nanometer scale regions requires the use of analysis techniques such as Atom Probe Tomography (APT) and Transmission Electron Microscopy (TEM). This presentation will discuss the role of APT and how elemental distributions vary depending on process conditions along with the challenges involved in sample preparation.

11:00am **PS+AS+EL+EM+SE-WeM10 Invited Talk-Future Stars of AVS Session: Three-Dimensional Imaging of Complex Oxide Interfaces***, Divine P. Kumah*[1]*,* North Carolina State University

Complex oxide materials have a wide range of exciting tunable electronic and magnetic phases including ferroelectricity and superconductivity. The ability to fabricate atomic layers of complex oxides has led to the formation of novel interfaces and heterostructures of scientific and technological interest. The functional properties are usually correlated to sub-Angstrom structural perturbations at these interfaces. In this talk, a non-destructive synchrotron X-ray three-dimensional imaging technique will be applied to understand thickness-dependent electronic and magnetic transitions which occur in rare-earth manganite films with thicknesses on the order of an atomic layer. We show that structural distortions arising due to the electrostatic interfacial boundary conditions of the thin films are related to their thickness-dependent phase transitions. Based on these results, we show that heterostructures can be designed by molecular beam epitaxy to tune the atomic-scale structure of the manganite films to achieve robust ferromagnetism in atomically-thin layers. These results have important implications for the design of oxide-based spintronic devices and provide an important pathway for the realization of novel functional materials.

11:20am **PS+AS+EL+EM+SE-WeM11 Invited Talk-Future Stars of AVS Session: lluminating Physics of Magnetron Sputtering Discharges***, Matjaz Panjan*[2]*,* Jozef Stefan Institute, Slovenia

Magnetron sputtering is an established plasma technology for the deposition of thin films. In general, the technique is classified by the voltage supplied to the cathode; this can be continuous (DCMS), pulsed (HiPIMS) or oscillatory (RFMS). The distinction is also made with respect to the geometry of the magnetron source (e.g., circular, linear, cylindrical) and the magnetic field configuration (balanced or unbalanced). Despite the differences in the cathode operation, geometry and, magnetic field configuration, the underlying principle that forms dense magnetron plasma is the same. The central feature of magnetron sources is a crossed magnetic and electric field arrangement, which captures electrons close to the cathode. In such configuration, electrons gyrate around the magnetic field lines, bounce from the electric field of the sheath and drift in the azimuthal direction. The entrapment of electrons increases the plasma density close to the cathode (e.g., forming a ring-shaped plasma above the circular magnetron) and enhances the sputtering rate. Experiments using high-speed imaging and other techniques revealed that magnetron plasma is not azimuthally homogenous instead, it forms dense plasma structures called spokes. These structures have been extensively studied over the past few years and have changed our understanding of several physical processes in the magnetron discharges.

Spokes are observed for a wide range of discharge conditions, magnetron geometries and are an essential feature of all operational regimes [1-3]. They commonly form periodic patterns, have an arrowhead-like shape with an arrow pointing in the **E**×**B** direction, and travel with azimuthal velocities of several km/s. In the talk, I will present efforts to understand the physics of spokes and magnetron discharges in general. In particular, I will discuss spatial distribution of the plasma potential [4] and the influence it has on the transport of charged particles [5], sputtering process and overall sustainability of the discharge. I will demonstrate that electric fields associated with spokes cause localized re-energization of electrons and thus help to sustain magnetron discharge. Spokes also influence energy and spatial distribution of ions and therefore indirectly affect the thin film growth.

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[2] A. Ehiasarian *et al.,Appl. Phys. Lett.*, **100** (2012) 11410

[3] M. Panjan *et al.*, *Plasma Sources Sci. Technol.*, **24** (2015) 065010

[4] M. Panjan and A. Anders, *J. Appl. Phys.***121** 063302 (2017)

[5] M. Panjan *et al.*, *Plasma Sources Sci. Technol.,* **23** (2014) 025007

11:40am **PS+AS+EL+EM+SE-WeM12 Peter Mark Memorial Award: Plasma-bio Interactions: Investigating Mechanisms to Enable New Applications***, Peter Bruggeman*[3]*,* University of Minnesota **INVITED**

Cold non-equilibrium atmospheric pressure plasmas (CAPs) have received a lot of attention in the last decades due to their huge potential for biomedical applications including wound healing, cancer treatment, dental treatments and disinfection and decontamination of heat sensitive materials [1]. These applications are due to the near ambient gas temperature at which CAPs can be produced and their high reactivity, involving the production of numerous reactive oxygen and nitrogen species [2]. Many applications require controlled interactions of plasma with bacteria, virus and mammalian cells or tissue that enable selectivity between healthy and cancer cells or in the treatment of bacteria on healthy tissue or food samples for which off target effects needs to be minimized. A controlled selectivity might be the greatest challenge for these applications and requires a detailed understanding of the underlying plasma-bio-interaction mechanisms. In this framework, my group in collaboration with microbiologists has performed detailed studies of the interactions of CAP with virus, bacteria and mammalian cells. Our research shows that controlling the gas phase plasma chemistry can lead to significant different biological responses of the living organisms [3-6]. The outcomes of these studies allow unraveling chemical pathways responsible for plasma-bio interactions and linking plasma kinetics to plasma-bio interactions. These insights are of invaluable importance for the development of applications in the field of plasma medicine.

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[5] G. Nayak, H.A. Aboubakr, S.M. Goyal and P.J. Bruggeman, Plasma Process. Polym. **15**, 1700119 (2018)

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Acknowledgements

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[1] **Future Stars of the AVS**

[2] **Future Stars of the AVS**

[3] **Peter Mark Memorial Award Winner**

Actinides and Rare Earths Focus Topic
Room 202C - Session AC+AS+SA-WeA

Chemistry and Physics of the Actinides and Rare Earths

Moderators: Krzysztof Gofryk, Idaho National Laboratory, Ladislav Havela, Charles University, Prague, Czech Republic, David Shuh, Lawrence Berkeley National Laboratory

3:00pm **AC+AS+SA-WeA3 Bond Distance Variations for Lanthanide and Actinide Compounds and its Implication***, **Tsuyoshi Yaita**,* Japan Atomic Energy Agency, Japan*; S. Suzuki, T. Kobayashi, H. Shiwaku,* Materials Sciences Research Center, Japan Atomic Energy Agency, Japan **INVITED**

Lanthanide and actinide are f-electron filling series and the properties of the series on their chemical behavior are very similar if valence states are same, while an electronic configuration of the inner shell for each element is slightly different compared to the similarity in size, and the value of special elements such as Nd and Dy used as neodymium magnet is high in the use of high-tech products. Regarding actinides series, radiotoxic Am is paid for attention in the geological disposal of radioactive waste and the R&D for partitioning and transmutation technique is performed. Accordingly, intra-series separation for lanthanide and actinide with similarity in chemical behavior would be quite important for the recovery of noble metal used as high-tech parts and treatment of high-level waste prior to geological disposal, resulting that the development of useful separation system could improve economic efficiency and reduction of environmental load.

On these backgrounds, we focus on the intra-series separation for lanthanide and actinide, especially, the relationship between variation of separation efficiency in the series and systematics of structure and electronic structure, and then, we try to propose new separation concept. Especially, in this talk, we talk about the variation of hydration or complex bond distances for trivalent actinide and lanthanide series based on X-ray crystallography and EXAFS and the interpretation based on the SX-XAS/XES and theoretical calculation.

4:20pm **AC+AS+SA-WeA7 Spectroscopic Studies of Trivalent Actinide Coordination***, **Benjamin Stein**, M.G. Kerlin, A.L. Morgenstern, E. Batista, S.E. Bone, S.K. Cary,* Los Alamos National Laboratory*; J. Lezama Pacheco,* SLAC National Accelerator Laboratory*; S.A. Kozimor, P. Yang,* Los Alamos National Laboratory **INVITED**

Radioisotopes have a rich history in medicine, with their use dating back to the earliest studies of radioactivity. Only recently, however, have α-particle emitting radionuclides been considered for medical applications. Targeted alpha therapy utilizes the unique properties of α-emitting radionuclides to selectively kill cancer cells, with the short range of α-particles causing minimal collateral damage to nearby healthy cells. Actinium-225 (^{225}Ac) has been identified by the Department of Energy Isotope Program Long Range plan as an isotope of high national interest for targeted alpha therapy, due to its favorable half-life (10 days) and 4 α-emissions in the decay chain. However, if the ^{225}Ac is not securely bound to the targeting vector this effectiveness results in very high toxicity to off-target (i.e. healthy) cells. Due to the high radioactivity and limited supply of all actinium isotopes, very little fundamental chemistry is known about this elusive element. Utilizing the unique radiological facilities at Los Alamos, we have been able to use microscopic amounts (~30 micrograms) of the longer-lived isotope actinium-227 (half-life of 22 years) for chemical studies. Utilizing this isotope, we have developed handling and containment techniques to perform "classic" spectroscopic and chemical studies in support of developing actinium chelates to advance the use of ^{225}Ac in targeted alpha therapy. During these studies of actinium coordination chemistry we have also made comparisons with the more "traditional" trivalent actinides, in particular americium and curium. We will discuss our latest EXAFS, NMR, and computational results on these difficult to handle elements by presenting a comparison of acetate and phosphonate binding, and how this informs chelator development.

5:00pm **AC+AS+SA-WeA9 Speciation of Rare Earth Elements in Coal Harvesting Byproducts***, **Xu Feng**, M. Council-Troche, J.R. Morris, A. Noble, R.-H. Yoon,* Virginia Polytechnic Institute and State University

Rare earth elements (REEs) are critical for the development of renewable energy resources, national security, and advanced manufacturing. With the recent closure of the rare earth mine in California, the U.S. relies entirely on foreign imports mainly from China, which poses serious economical and national security concerns. According to a study commissioned by the National Energy Technology Laboratory (NETL), the U.S. coal and coal byproducts contain ~11 million metric tons of recoverable REEs, only a small fraction of which could satisfy the domestic need [1].

Recent USGS studies showed that the REEs in U.S. coals are preferentially partitioned to clay minerals [1], suggesting that the clay byproducts may be a major source of the critical materials. Ion-adsorbed REEs in clay appear to exist as two distinct forms: (1) ionic species adsorbed by coulombic attraction which is thought to be the primary form in REE-adsorbed clay deposits in South China, and (2) colloidal REEs formed by hydrolysis, each requiring a unique extraction strategy. However, the conditions under which the ion-exchange clays were formed in the U.S. coals and accompanying mineral matter may be different from those for the South China ion-adsorption clays, and the specific speciation of REEs in U.S. coal materials is currently unknown. It is, therefore, critical to study the fundamental mechanisms by which REEs are adsorbed on clay minerals in aqueous media to develop effective targeted extraction strategies.

In this work, X-ray photoelectron spectroscopy (XPS) was used to characterize the chemical state of representative light and heavy rare earth elements on artificial REE-adsorbed clay samples. Characteristic REE $3d_{5/2}$ features of the artificial clay sample, including the peak position of the two multiplet-split components, the magnitude of the multiplet splitting and the intensity ratio of each multiplet-split component, were compared to those of the high-purity REE standards such as $REE(OH)_3$, REE_2O_3 and $REECl_3$ to provide insight into the identification of REE speciation on the artificial sample. XPS results suggest that $REE(OH)_3$ is the primary REE species on the artificial REE-adsorbed clays. Furthermore, X-ray Adsorption Spectroscopy (XAS) was used to probe the speciation of representative light and heavy REEs in natural coal and coal byproduct samples by comparing the oxidation states and specific bonding environments to those of REE standard materials.

[1] Bryan, R. C., D. Richers, H.T. Andersen, and T. Gray, "Assessment of Rare Earth Elemental Contents in Select United States Coal Basins," Document No: 114-910178-100-REP-R001-00, January 2015.

5:20pm **AC+AS+SA-WeA10 Exotic Electronic Properties of Strongly Correlated Compounds $NpPd_3$ and $PuPd_3$***, **Krzysztof Gofryk**,* Idaho National Laboratory*; J.-C. Griveau, E. Colineau,* Institute for Transuranium Elements*; K.A. McEwen,* University College London*; W.J. Nellis,* Harvard University*; J.L. Smith,* Los Alamos National Laboratory

Actinides are characterized by the coexistence of localized and itinerant (delocalized) 5*f*-states near the Fermi energy. This dual nature of the 5*f*-electrons leads to many complex phenomena that are observed in these strongly correlated materials, spanning magnetic ordering, heavy-fermion ground state, unconventional superconductivity, and/or "non-Fermi liquid" state. The electronic properties of the strongly correlated electron systems are related to the formation, near the Fermi level, of a narrow band with large density of states and in spite of intensive theoretical and experimental efforts their nature is still not well understood. This behavior is well emphasized in $AnPd_3$ (*An*-U, Np, Pu) system. UPd_3 crystalizes in the hexagonal crystal structure and shows four phase transitions below 7.8 K, attributed to a succession of antiferroquadrupolar orderings of the uranium ions localized on the quasi-cubic sites of the *d*hcp structure. Depending on a heat treatment, $NpPd_3$ crystalizes in hexagonal and cubic crystal structures. The hexagonal $NpPd_3$ (h-$NpPd_3$) exhibits two transitions at 30 and 10 K. It has been suggested that the low temperature transition might be due to ordinary antiferromagnetic ordering while the high temperature one might be caused by a quadrupolar order. The cubic $NpPd_3$ (c-$NpPd_3$) orders antiferromagnetically below 52 K and the magnetic and transport measurements suggests that the transition is first order. $PuPd_3$ crystalizes in the cubic structure and shows an antiferromagnetic order below 24 K. To explore the influence of electronic correlations on the physical properties in the $AnPd_3$ system, here we present our detailed magnetic, thermodynamic, and transport studies of $NpPd_3$ and $PuPd_3$.We show that all results obtained present characteristic behaviors of 4*f*- and 5*f*-electron strongly correlated materials. The magnitude and overall temperature dependence of the electrical resistivity, magnetostesitivity, Hall and Seebeck effect, and heat capacity of $NpPd_3$ and $PuPd_3$ are archetypal of materials with Kondo interactions. Our measurements also reveal an unusual magnetic ordering in c-$NpPd_3$. At T_N, the specific heat exhibits an extremely large peak [as large as 1000 J/(mol K)] and the magnetic susceptibility shows a clear jump. The transport properties of c-$NpPd_3$ indicate a dramatic reconstruction of the electronic structure at the Néel temperature, probably accompanied by a large change in the Fermi surface topology, which shows up as pronounced anomalies at this temperature in the electrical resistivity, the magnetoresistivity, and the

Seebeck and the Hall coefficient. We will discuss implications of these results.

Applied Surface Science Division
Room 204 - Session AS+SE-WeA

Industrial and Practical Applications of Surface Analysis

Moderators: Jeffrey Fenton, Medtronic, Svitlana Pylypenko, Colorado School of Mines

2:20pm **AS+SE-WeA1 Identification of Unknown Contaminants in Industrial Applications Using MS/MS in Combination with High Resolution Mass Spectrometry**, *A. Pirkl,* ***Julia Zakel****, D. Rading,* IONTOF GmbH, Germany*; N.J. Havercroft,* IONTOF USA*; S. Kayser, H. Arlinghaus, R. Moellers, E. Niehuis,* IONTOF GmbH, Germany

The fast and reliable characterisation of unknown contaminants in quality control procedures is crucial in many industrial areas to understand manufacturing errors and avoid production downtime. TOF-SIMS nowadays plays an important role in this area especially due to its fast imaging capabilities that enable the acquisition of chemical surface images with a lateral resolution in the 100 nm range.

However, molecular identification of unknown substances 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 Exactivemass 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.

Different applications ranging from polymers to metals will be presented with a focus on the identification of unknown substances by MS/MS in combination with high resolution mass spectrometry. Furthermore dedicated measurement modes and strategies that can be applied to different forms of contaminants will be presented. The use of databases will be showcased which further assists and confirms the results of a manual data evaluation.

[1] The 3D OrbiSIMS – Label-Free Metabolic Imaging with Sub-cellular Lateral Resolution and High Mass Resolving Power, Passarelli et al., Nature Methods, 2017, 14(12):1175-1183, DOI 10.1038/nmeth.4504.

2:40pm **AS+SE-WeA2 ToF-SIMS Analysis of Glass and Glass Coatings***,* ***Christine Mahoney****,* Corning Inc.

Many think of glass as being an inert material. However, glass contains many reactive alkalis and other elements that can interact and diffuse into solutions or into coatings. These alkalis tend to decrease the chemical durability of the glass itself, and can play a key role in accelerating corrosion and delamination mechanisms involving the glass. How we manufacture and process the glass plays a significant role in its chemical durability and reactivity. The reactivity of a glass surface can be particularly problematic for pharmaceutical applications, where glass delamination in vials and/or drug interactions with glass constituents can potentially occur. Here we present an overview of ToF-SIMS research at Corning involving the analysis of glass surfaces and their associated coatings. Both organic and inorganic applications will be discussed, using a wide range of tools for analysis.

3:00pm **AS+SE-WeA3 Problem Solving with Valence Band Spectroscopy and SIMS MS/MS***,* ***Steven Pachuta****, D.M. Poirier,* 3M Company **INVITED**

Surface chemistry is often key to the performance of materials like films, coatings, and adhesives. Controlling and understanding surface chemistry is therefore critical to manufacturers. X-ray photoelectron spectroscopy (XPS) is the workhorse in industrial surface characterization laboratories, followed closely by time-of-flight secondary ion mass spectrometry (ToF-SIMS). XPS survey spectra provide quantitative elemental information on surfaces, and XPS high energy-resolution spectra can give information on chemical states. ToF-SIMS, in general, gives even more specific surface chemical information, such as the identities of polymer additives and surface contaminants.

This presentation will describe efforts to increase the chemical specificity of both XPS and ToF-SIMS for organic species, especially polymers. The XPS valence band region contains a complex fingerprint which is highly dependent on molecular structure. By using databases in combination with multivariate methods such as principal component analysis (PCA) and partial least squares (PLS), a surprising degree of information can be extracted from valence band spectra of unknown materials.

The fact that many real-world surfaces comprise a mixture of components is a recurrent frustration in industrial surface characterization. ToF-SIMS analysts have long envied their GC/MS and LC/MS counterparts, who have the luxury of separating mixtures before doing mass spectrometry. The recent commercial availability of tandem mass spectrometry (MS/MS) on ToF-SIMS instruments has gone some way towards addressing the mixture problem and has increased the ability of ToF-SIMS to identify unknown materials. Examples will be presented.

4:20pm **AS+SE-WeA7** ***Surface and In-depth XPS Characterization of Liquid and Cured Control Release Additives (CRAs) Used in Silicone-Based Release Coatings****,* ***Brian Strohmeier****, K. Rhodes, R. Munigeti, J. Orlowski,* Avery Dennison Corporation

Silicone-based release coatings are used in a wide variety of commercial applications including: release liners for removable pressure sensitive adhesive laminates and tapes, release papers and polymer films, non-stick packaging, and other products where a specific force of peel separation is required between two different film materials during processing or storage. Typical industrial silicone-based release coatings consist of UV or heat cured mixtures of silicone compounds and controlled release additives (CRAs). CRAs commonly contain proprietary mixtures of functionalized silanes, siloxanes, and silica, plus a variety of other organic components. The release properties of silicone-based release coatings depend highly on the distinct types and relative amounts of the silicone compounds and CRAs used in the cured mixture. Therefore, it is of great interest to quantitatively characterize the silicone and CRA components on the surface of silicone release coatings for improved product and process development as well as problem-solving related to release issues. In this study, a variety of commercial CRA products were characterized by gel permeation chromatography (GPC) for bulk molecular weight distribution information and by X-ray photoelectron spectroscopy (XPS) for surface composition and chemistry. The CRA materials studied had vapor pressures that allowed successful XPS characterization in the liquid state. Surprisingly, the CRA liquids could even be sputtered and/or depth profiled using argon cluster ions, whereas sputtering with monatomic argon ions resulted in XPS chemical state changes caused by ion beam induced sample damage. The CRA materials were characterized by XPS and argon cluster ion sputtering/depth profiling in the pure liquid state and in solid heat cured release coating mixtures with polydimethyl siloxane (PDMS). The high resolution Si 2p XPS spectra obtained for cured silicone release coatings of known composition could be peak-fitted into separate CRA and PDMS components to produce a quantitative calibration curve for evaluating release coatings with unknown CRA/silicone compositions.

4:40pm **AS+SE-WeA8 Differentiating Silicones Using SIMS***,* ***Paul Vlasak****, M.L. Pacholski,* The Dow Chemical Company

The unique properties of poly(dimethylsiloxane), also known as PDMS or silicone, have allowed PDMS-based materials to proliferate in modern industry. A huge variety of applications using PDMS have been developed including structural adhesives, release agents, optical components, lubricants, anti-foam agents, and potting agents to name a few. Considering the omnipresence of PDMS in industrial settings along with its low surface energy and tendency to migrate, it comes as no surprise that PDMS is frequently encountered in industrial surface analysis laboratories. Because PDMS is readily detected and easily recognized by its characteristic fragmentation pattern, SIMS is well suited to identifying the presence of silicones on a wide range of materials.

In some instances, the analyst expects to find PDMS on a sample surface. For example, the PDMS transferred from a silicone release liner onto an adhesive may be of interest. In other instances, PDMS can be encountered as an unexpected contaminant, perhaps interfering with adhesion or causing defects in a coating or painting operation. In either case, besides its mere presence, the structural details of the PDMS may be important to understanding the behavior of the adhesive/release system or discovering the actual source of a contaminant amongst multiple possibilities.

From a pragmatic standpoint, the current work explores how molecular weight, endgroup type, and other structural factors influence PDMS fragmentation patterns through the use of well-characterized reference materials. The effects of instrument-related parameters as well as film thickness and substrate type will also be considered to the extent these factors influence the spectra obtained.

5:00pm **AS+SE-WeA9 Uranium Particles Analysis and Imaging Using ToF-SIMS for Source Identification***, Juan Yao, E. Krogstad, S. Shen, Z.H. Zhu, X-Y. Yu,* Pacific Northwest National Laboratory

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is a highly surface sensitive analytical tool. It offers excellent limits of detection (LODs) of part per million with sub-micron spatial resolution. Besides determining isotopic ratios of radioactive materials, ToF-SIMS has the advantage of providing full mass spectra with m/z up to 2000 Da, allowing the detection of chemical signatures in a material. This latter feature is very attractive to identify the source of uranium and other radioactive materials in single particles. We analyzed three different NIST standard reference materials with varied concentrations of uranium in this study. Samples are in the form of glass wafers and particles deposited on a substrate. By applying spectral principal component analysis (PCA), the SIMS mass spectra obtained from the same type of NIST sample show consistent features; regardless of the sample form. Furthermore, a blind test was conducted using a mixture consisting of particles from all three NIST materials. Our spectral PCA results illustrate that ToF-SIMS can be a useful tool to differentiate particles of different origins and potentially applicable for signature identification in single particles. In addition, scanning electron microscopy (SEM) was applied to complement the SIMS imaging for correlative analysis [1]. It is beneficial to use SEM to obtain particle morphological information. However, SEM lacks the sensitivity in single particle elemental analysis compared to ToF-SIMS. Our work demonstrates that ToF-SIMS is a powerful tool for analysis of individual radioactive particles to fulfill nuclear safeguards and forensic missions.

5:40pm **AS+SE-WeA11 Application of X-ray Photoelectron Spectroscopy to Degradation Studies of Electrodes in Fuel Cells and Electrolyzers***, Kateryna Artyushkova,* University of New Mexico*; N. Danilovic,* Lawrence Berkeley Lab, University of California, Berkeley*; C. Capuano,* Proton on site*; A. Serov,* Pajarito Powder LLC*; P. Atanassov,* University of New Mexico

The stability of materials used used in anodes and cathodes in fuel cells and electrolyzers is a critical factor for practical industrial applications. To improve the longevity, it is important to link the chemical structure to degradation mechanisms and changes in the surface composition of the catalyst on the electrodes. Application of x-ray photoelectron spectroscopy (XPS) to probe structure of catalytic materials and their degradation is becoming an important analytical approach due to its accessibility and quantitative chemical information provided. This talk will present several examples of application of high-resolution XPS for analysis of the chemistry of electrodes and changes that are occurring during operation in several technological platforms, such as proton-exchange membrane fuel cells (PEMFCs), alkaline membrane fuel cells (AEMFC), direct methanol fuel cells (DMFC), direct hydrazine fuel cells (DHFC) and water electrolyzers (WE).

Biomaterial Interfaces Division
Room 104B - Session BI+AC+AS+HC+NS+SS+TF-WeA

Current and Future Stars of the AVS Symposium II

Moderator: David Boris, U.S. Naval Research Laboratory

2:20pm **BI+AC+AS+HC+NS+SS+TF-WeA1 Medard W. Welch Award Lecture: A Surface Scientist's Journey from Small Molecules to Biomolecules and Biomaterials***, David G. Castner*[1]*,* University of Washington **INVITED**

Surface science plays an important role in a wide range of research and development areas such catalysis, biomaterials, microelectronics, clean energy and corrosion. The toolbox of surface scientist allows us to easily move across research topics and make significant impacts in both industrial and academic settings. The typical surface scientist is an expert in multiple techniques, surface modification, sample preparation/handling and instrumentation. We have all benefited from the significant and numerous advances that have occurred in the past 40 years in terms of improved instrumentation, introduction of new techniques and development of sophisticated data analysis methods, which has allowed us to perform detailed analysis of increasing complex samples. For example, comprehensive analysis of surfaces and surface immobilized molecules with modern surface science instrumentation provides an unprecedented level of detail about the immobilization process and the structure of the immobilized molecules. Results from x-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), near edge x-ray absorption fine structure (NEXAFS), surface plasmon resonance (SPR) and quartz-crystal microbalance with dissipation (QCM-D) biosensing, atomic force microscopy, and sum frequency generation (SFG) vibrational spectroscopy combined with computation methods such as molecular dynamic (MD) and Monte Carlo (MC) simulations provide important information about surface chemistry and structure. However, even with the advances that have been achieved with these powerful surface science techniques, there still remain many significant challenges for surface scientist. These include characterizing the surface chemistry and structure of nanoparticles, determining the atomic level structure of complex molecules bound to surfaces, 3D imaging of samples, and improved sample preparation methods that maintain materials in a relevant state when using ultra-high vacuum based analysis techniques.

This talk will discuss my adventures as a surface scientist starting from chemisorption and reactivity studies of small molecules on single crystal surfaces followed by industrial catalysis research and eventually moving to biomedical surface analysis with side ventures into areas such as clean energy. It has been an exciting journey and I will use it to provide some examples of the multidisciplinary nature of surface science as well as discuss opportunities for addressing future challenges.

3:00pm **BI+AC+AS+HC+NS+SS+TF-WeA3 Invited Talk-Future Stars of AVS Session: Making, Studying, and Designing Hierarchically Structured Soft Materials***, Keith A. Brown*[2]*,* Boston University

Nature realizes extraordinary materials by structuring them precisely from the molecular scale to the macroscopic scale. While nature may have perfected this process over evolutionary time scales, synthetically recapitulating this level of control is tremendously difficult due to the large number of length scales involved and our limited knowledge of interactions between these scales. Faced with the daunting challenge of synthetically realizing soft hierarchical materials, we have adopted a three pronged strategy to: (1) make structures with control from the molecular scale to the macroscopic scale by directing bottom-up growth processes with top-down control, (2) learn how the properties of such materials emerge from their hierarchical structure, and (3) design the best performing structures using novel approaches borrowed from machine learning and autonomous research. In this talk, we will on report recent progress in this complementary areas of making, studying, and designing hierarchical materials. In particular, we will focus on two major classes of materials, nanoparticle-based structures where the assembly and organization of particles leads to emergent mechanical properties at the bulk scale and polymer-based materials where we are connecting the synthesis, patterning, and properties of polymer structures across scales. In addition to lessons about the fundamental properties of hierarchically organized soft matter, we will highlight the synergies possible when combining, synthesis, detailed characterization, and advances in materials design.

3:20pm **BI+AC+AS+HC+NS+SS+TF-WeA4 Invited Talk-Future Stars of AVS Session: Vapor Phase Infiltration for Transforming Polymers into Hybrid Materials: Processing Kinetics and Applications***, Mark Losego*[3]*,* Georgia Institute of Technology

Vapor phase infiltration (VPI) is an emerging processing technology for infusing polymers with inorganic constituents to create new organic-inorganic hybrid materials with novel chemical, electrical, optical, and/or physical properties. These new hybrid materials have demonstrated applications including chemical separations, photovoltaics, and microelectronics patterning. This talk will focus on our development of a fundamental VPI processing kinetics phenomenology to create a pathway for rational design of material composition and structure. By measuring VPI compositional profiles as a function of space or time and temperature, we can extract fundamental energy barriers for the sorption, diffusion, and reaction processes and delineate amongst different rate limiting steps. In our materials development, we often find that partial infiltration of a polymer film, fiber, or foam is sufficient to impart desired properties; so rational design of the infiltration kinetics can enable desired performance without waste in processing time or materials. Here, we will demonstrate several examples including our work to create chemically insoluble polymers and membranes. We find, for example, that infiltration depths of about 0.75 microns are sufficient to yield PMMA chemically insoluble in organic solvents regardless of whether it is in a thin film geometry or a macroscopic plexiglass object of centimeters in dimension. In PIM-1 membranes used for chemical separations, we find that we can achieve > 30 wt% inorganic loading with a single infiltration exposure. After

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[1] **Medard W. Welch Award Winner**

[2] **Future Stars of the AVS**

[3] **Future Stars of the AVS**

infiltration, these membranes become stable in new separations solvents that previously swelled and/or dissolved the polymer.

(Submitted for the Future Stars of the AVS Symposium.)

4:20pm **BI+AC+AS+HC+NS+SS+TF-WeA7 Invited Talk-Future Stars of AVS Session: Surface Preparation Methods for the Selective Oxidation of Ethanol to Acetaldehyde over TiO_2/Au(111)***, **Ashleigh Baber**[1], D.T. Boyle, J. Wilke, V. Lam, D. Schlosser,* James Madison University

Obtaining a molecular-level understanding of the reaction of alcohols with heterogeneous model catalysts is critical for improving industrial catalytic processes, such as the production of hydrogen from alcohols. The use of reducible oxides provides a source of oxygen on Au(111) for the reaction of ethanol, which is easily regenerated in the presence of an oxygen background. The redox chemistry of small alcohols, including methanol and propanol, has been studied on Au(111) supported TiO_2 nanoparticles, yet the active site for the chemistry has not yet been elucidated. Depending on the surface preparation conditions, Au(111) supported TiO_2 nanoparticles react with small alcohols to form either reduced and oxidized products. The desire to selectivity form oxidized or reduced products merits an investigation of alcohol reactivity over differently prepared TiO_2/Au(111) surfaces. In this work, a systematic study of ethanol reactivity over several TiO_2/Au(111) surfaces elucidates the effect of surface conditions on the selectivity of the reaction between ethanol and TiO_2/Au(111). The reactivity of the surface for ethanol oxidation was altered by controlling the oxidation state of TiO_x (x<2). Atomic force microscopy (AFM) provides information regarding the structure of the Au(111) supported TiO_2 nanoparticles and ultrahigh vacuum temperature programmed desorption (TPD) monitors the selectivity of the reaction between ethanol and TiO_2/Au(111). The presence of TiO_2 nanoparticles on Au(111), ~25 nm in diameter, led to the catalytic conversion of ethanol to acetaldehyde at temperatures greater than 400 K. Low coverages of fully oxidized TiO_2 nanoparticles on Au(111) are active for the selective oxidation of ethanol to form acetaldehyde.

4:40pm **BI+AC+AS+HC+NS+SS+TF-WeA8 Invited Talk-Future Stars of AVS Session: Single Atom Catalysis: An Atomic-Scale View***, **Gareth Parkinson**[2],* TU Wien, Austria

Single-atom catalysis is a rapidly emerging area of research that aims to maximize the efficient usage of precious metals through ”single atom” active sites. Although catalytic activity has been demonstrated for several single-atom catalyst systems, an inability to accurately characterize the catalyst based on single atom active sites ensures that that the field remains controversial, and little is really known about how a single atom adsorbed on a metal oxide support catalyzes a chemical reaction. In this lecture, I will describe how we are addressing the crucial issues of stability and reaction mechanism using a surface science approach. The work is based on the magnetite (001) surface, which exhibits an unusual reconstruction based on subsurface cation vacancies.

The surface stabilizes ordered arrays of metal adatoms (of almost any variety) with a nearest neighbor distance of 0.84 nm to unprecedented temperatures as high as 700 K. Crucially, because the geometry of the adatoms is uniform and precisely known, reactivity experiments are performed on a well-defined model system, and theoretical calculations can be performed to shed light on the mechanisms at work. Several examples of our recent work will be used to illustrate the trends discovered to date, including how strong CO adsorption destabilizes Pd and Pt adatoms leading to rapid sintering, and how extraction of lattice oxygen from the metal-oxide is central to catalytic activity in the CO oxidation reaction.

5:00pm **BI+AC+AS+HC+NS+SS+TF-WeA9 Invited Talk-Future Stars of AVS Session: Multimodal Chemical and Functional Imaging of Nanoscale Transformations Away from Equilibrium***, **Olga Ovchinnikova**[3],* Oak Ridge National Laboratory

The key to advancing energy materials is to understand and control the structure and chemistry at interfaces. While much of the dynamic chemistry can be studied on macro-scale systems, there is a lack of means to localize chemical measurements and correlate them to nanoscale structure of the material. Through a unique merger of advanced scanning probe microscopy and mass spectrometry techniques rooted in innovative data processing and control algorithms, we are now able to understand the interplay between chemical and physical functionality at the fundamental length using multimodal chemical imaging. This multimodal imaging transcends existing techniques by providing nanoscale structural imaging with simultaneous quantitative nanomechanical properties and quantitative chemical analysis. In this talk I will discuss how we have developed and used this capability to visualize dynamic material transformations at interfaces, to correlate these changes with chemical composition, and to distil key performance-centric material parameters. One exciting capability is that the AFM can be used to drive materials away from equilibrium at the nanoscale with highly localized electric fields. This allows field confinement effects on localized chemistry in materials to be locally probed, especially at interfaces. This in turn yields direct information on key energy related questions such as electron and ion motion distribution and transport at and between interfaces. We have applied this approach to the study of systems and processes that underlie energy capture, conversion and storage, including photovoltaics and oxide ferroelectrics, which have historically eluded comprehensive understanding of the mechanisms behind the spatially heterogeneous interfacial chemistry and its link to material performance. Overall, I will focus on ways to unlock the mystery of active interface formation through intertwining data analytics, nanoscale elemental and molecular characterization, with imaging; to better grasp the physical properties of materials and the mechanistic physics-chemistry interplay behind their properties.

5:20pm **BI+AC+AS+HC+NS+SS+TF-WeA10 Invited Talk-Future Stars of AVS Session: Expanding the Structural Toolkit to Characterize Heavy Actinide Complexes***, **Rebecca Abergel**[4],* Lawrence Berkeley Lab, University of California, Berkeley*; G. Deblonde, A. Mueller, P. Ercius,* Lawrence Berkeley National Laboratory*; A.M. Minor,* Lawrence Berkeley Lab, University of California, Berkeley*; C.H. Booth, W.A. de Jong,* Lawrence Berkeley National Laboratory*; R. Strong,* Fred Hutchinson Cancer Research Center

Structural characterization of actinide elements from actinium to einsteinium can be a challenging task due to the high radioactivity and limited availability of some of the isotopes of interest. However, significant work is needed to address a certain lack of understanding of the fundamental bonding interactions between those metal centers and selective ligands. Such understanding presents a rich set of scientific challenges and is critical to a number of applied problems including the development of new separation strategies for the nuclear fuel cycle, 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 as well as transmission electron microscopy and electron energy loss spectroscopy to investigate specific heavy actinide coordination features. Using simple inorganic complexes but also strong hard oxygen-donor ligands as well as more elaborate higher molecular weight protein assemblies allows the differentiation of heavy actinide species even when limited to minute amounts of materials. Innovative structural characterization approaches based on X-ray absorption, X-ray diffraction and electron microscopy that were applied to series of isostructural systems and used to derive coordination trends in the later 5*f*-element sequence will be discussed.

5:40pm **BI+AC+AS+HC+NS+SS+TF-WeA11 Invited Talk-Future Stars of AVS Session: Trends in Adsorbate Interactions with Bimetal Surfaces***, **Liney Arnadottir**[5], L.H. Sprowl,* Oregon State University

Surface chemistry plays an important role in a large range of applications and technologies, such as catalysis and electrocatalysis, device fabrication through film growth, and degradations through oxide formation, carbonization, and corrosion. Bimetal surfaces are of increasing interest for single atom catalysis and corrosion resistance of alloys. Previous studies have shown correlations between adsorbate interactions and d-band shifts for different metals as well as for alloying effects of metal sandwich structures, but for mixed metal surfaces the nature of the adsorption site can change (ensemble effect) as well as the number of electrons in the surface layer which effects the d-band center. Here we explore correlations of adsorbate interactions with mixed metal surfaces through density functional theory calculations of adsorbate interactions with different facets, (100) and (111), of pure Ni and eleven Ni-based surface alloys as well as Ni in different host metal. We find that the addition of surface alloying atom has little effect on the binding of CO and C but C binding varies for different facets. On the other hand, O binding is highly dependent on the alloying element due to ensemble effect. This has an

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[1] **Future Stars of the AVS**

[2] **Future Stars of the AVS**

[3] **Future Stars of the AVS**

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[5] **Future Stars of the AVS**

interesting effect on the predicted reaction energies of CO dissociation which is endothermic on the (111) facet and exothermic on the (100) facet governed by C interactions but the changes in the reaction energy within each facet are mostly governed by the ensemble effect on O adsorption. The relationship between the formation energy of the mixed metal surface and adsorbate interactions will also be discussed.

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic

Room 202A - Session SA+AS+MI-WeA

Hard X-Ray Photoemission for Probing Buried Interfaces

Moderators: Zahid Hussain, Advanced Light Source, Lawrence Berkeley National Laboratory, Olivier Renault, CEA-LETI, France

2:20pm **SA+AS+MI-WeA1 Element-resolved Electronic Band Structure of Ga(Mn)As Measured by Standing-wave Hard X-ray Angle-resolved Photoemission*, Slavomir Nemsak,*** Advanced Light Source, Lawrence Berkeley National Laboratory*; M. Gehlmann, C.-T. Kuo,* University of California, Davis*; T.-L. Lee,* Diamond Light Source Diamond House, Harwell Science and Innovation Campus*; L. Plucinski,* Forschungszentrum Juelich GmbH, Germany*; J. Minar,* University of West Bohemia*; C.M. Schneider,* Forschungszentrum Juelich GmbH, Germany*; C.S. Fadley,* University of California, Davis

Electronic band structure of the dilute magnetic semiconductor Ga$_{(1-x)}$Mn$_x$As was obtained using hard X-ray angle-resolved photoemission. The element- and site-sensitivity of the measurements was achieved by forming a strong X-ray standing-wave generated by Bragg reflection from the (111) atomic planes of both undoped GaAs and Mn-doped thin films. Due to the uneven occupancy of (111) planes by either Ga(Mn) or As atoms, the element-specific band structure can be obtained with a help of the SW modulation in core levels. Measured momentum- and element-resolved bulk electronic structure was compared to element-projected Bloch spectral functions with excellent agreement between experiment and theory. Apart from the site specific decomposition of the electronic structure, the SW measurements also confirmed a substitutional presence of Mn atoms at the Ga sites. This novel technique should be applicable to a broad range of complex materials.

2:40pm **SA+AS+MI-WeA2 Probing Surface Band Bending of Polar GaN by Hard X-ray Photoemission Combined with X-ray Total Reflection*, Shigenori Ueda,*** NIMS, Japan

GaN is known as a polar semiconductor due to an alternative stacking of Ga and N layers along the c-axis. Ohsawa *et al*. [1] showed the difference in valence band spectral shapes of the bulk Ga- and N-polar GaN single crystals by using polarization dependent hard X-ray photoemission spectroscopy (HAXPES). In general, HAXPES is a bulk-sensitive probe [2], and take-off angle (TOA) dependent of photoelectron gives depth information [3]. However, the decrease of the photoemission intensity occurs in lower TOA, and the valence band spectra depend on TOA [3] due to the matrix element effect [4].

In this work, HAXPES combined with X-ray total reflection was used to obtain a depth-resolved electronic structure instead of TOA dependent measurements. The change of incidence angle within 1 degree around the critical angle of X-ray total reflection drastically changes the attenuation length of X-ray in solids.

We have measured the core-level and valence band HAXPES spectra of commercially available bulk single crystalline GaN for Ga and N polar faces in the case of inelastic mean free path of 2.17, 3.73, and 7.69 nm. Undoped *n*-type GaN crystal with fine polished surfaces was used. For the Ga-polar face, large band bending behavior was observed, while the band bending was small for the N-polar face. The Ga 3s and N 1s core-level spectra also showed the polarity dependent band bending behavior. We found that GaN near the surface is degraded in both the polar faces. This result suggests that high quality single crystalline GaN with fine surface treatment is required for detecting the intrinsic electronic structure of GaN. Finally we note that HAXPES combined with X-ray total reflection is useful method for depth-resolved electronic structure measurements, since the data acquisition time in this method is 10 or more faster than that in TOA dependent measurement, and the matrix element effect is almost negligible in this method.

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3:00pm **SA+AS+MI-WeA3 Interfaces in Cycled Battery Electrodes: Insights from HAXPES Studies*, Julia Maibach,*** Karlruhe Institut of Technology (KIT), Germany **INVITED**

Rechargeable ion batteries such as lithium and sodium ion batteries generally consist of a negative electrode, a positive electrode and an ion conducting electrolyte. The contacts between the different materials are key to the electrochemical energy storage process and at the surfaces of the electrodes and at the interfaces to the electrolyte, reactions crucial to long-term, safe battery operation take place. Due to its surface and chemical sensitivity, photoelectron spectroscopy has therefore become a widely used tool to characterize and understand the processes and phenomena in these electrochemical energy storage systems.

Looking in more detail, a battery electrode itself is a complex system as it consists of many different components such as the active storage material, conductive additives as well as binders to keep the particles attached to a metal foil, which acts as a current collector. This complexity of mixed materials and morphologies further increases when the electrodes are cycled electrochemically due to the desired storage processes and due to reactions with the battery electrolyte leading to interface layer formation.

These highly complex systems of cycled battery electrodes bring new challenges when studied with photoelectron spectroscopy. In this presentation, observed peak shifts for cycled battery electrodes will be discussed in depth. Particular emphasis will be given to the buried interfaces. Here, hard x-ray photoelectron spectroscopy (HAXPES) is one of the few available techniques that can access the buried interface while maintaining the chemical information from the delicate battery interface layers. Based on HAXPES experiments, the role of the buried interfaces and their importance in both battery operation as well as in photoelectron spectroscopy characterization of cycled electrodes will be discussed.

Additionally, spectral changes due to electrode potentials as well as lithiation effects will be discussed. These strongly depend on the nature of the active material and therefore need to be considered carefully to achieve consistent data interpretation. Combining all presented effects, a strategy for photoelectron spectroscopy experiments on cycled battery electrodes will be proposed that takes buried interfaces into account.

4:20pm **SA+AS+MI-WeA7 Development of Ambient Pressure HAXPES and other HAXPES Measurements at SPring-8 for Buried Interface*, Yasumasa Takagi,*** Japan Synchrotron Radiation Research Institute (JASRI), Japan **INVITED**

A near ambient pressure photoelectron spectroscopy measurement that use with hard X-rays (AP-HAXPES) were conducted at the BL36XU of SPring-8. The AP-HAXPES system with a commercial differential pumping-type spectrometer (R4000 HiPP-2, Scienta Omicron Inc.) was installed in the beamline. The excitation light of 7.94 keV focused to a beam size of 20 µm x 20 µm on the sample surface was used. The standard aperture size at the top of the front cone in the spectrometer is a diameter of 300 µm. In this report, we replaced the front cone with our home-made one with an aperture diameter of 30 µm to increase the pressure limit in the AP-HAXPES measurement. Meanwhile, we have adapted the working distance of 60 µm in order not to perturb the gas environment at the sample surface.

We measured the XPS spectra of the Au(111) surface grown on a mica substrate under various gas pressures using the AP-HAXPES equipment. The intensity decay of the Au 4f spectra with an increasing gas pressure from 1 Pa to 100 kPa. Here we use “100 kPa” as the atmospheric pressure. The XPS measurement was not affected by the ambient gas at a pressure of 1 Pa. As the gas pressure increased, the signal intensity decreased because the photoelectrons were scattered by the ambient gas while passing through the sample to the detector. Although the signal intensity was very weak at the atmospheric pressure, the peaks of $4f_{5/2}$ and $4f_{7/2}$ can be detected. The signal-to-noise ratio can be improved by a prolonged acquisition time. The $4f_{7/2}$ and $4f_{5/2}$ peaks are clearly found in the spectrum at the atmospheric pressure in an acquisition time of 30 min. The Shirley background was subtracted from the spectrum, and the plots were fitted with a Voigt function. The curve fitting result shows that the energy difference between the $4f_{7/2}$ and $4f_{5/2}$ peaks is 3.7 eV and the intensity ratio $4f_{7/2}$:$4f_{5/2}$ is almost 4:3. These values are in good agreement with the standard value of the Au 4f peaks. Thus, a photoelectron spectroscopy under atmospheric pressure was successfully obtained using an aperture of 30 µm.

5:00pm **SA+AS+MI-WeA9 Operando HAXPES Investigations of La Manganite-based Resistive Memories**, ***Eugénie Martinez,*** CEA/LETI-University Grenoble Alpes, France; *BM. Meunier,* Univ. Grenoble Alpes, CEA, LETI & LMGP, CNRS, France; *DP. Pla,* Univ. Grenoble Alpes, LMGP, CNRS, France; *RRL. Rodriguez-Lamas,* Univ. Grenoble Alpes, LMGP, CNRS France; *MB. Burriel, CJ. Jimenez,* Univ. Grenoble Alpes, LMGP, CNRS, France; *JPR. Rueff,* Synchrotron SOLEIL, France; *Y. Yamashita, S. Ueda,* NIMS, Japan; *O.J. Renault,* CEA/LETI-University Grenoble Alpes, France

The use of perovskite oxides in resistive random access memories (RRAMs) is considered for the next generation of non-volatile memories (NVMs) [1]. Indeed, their highly tunable ionic and electronic transport properties open new possibilities for multilevel storage capacity. In particular, manganese oxides, such as LaMnO$_{3+d}$ (LMO), are among the most promising candidates [2].The switching mechanism is related to oxygen transport, yielding to the creation and annihilation of oxygen vacancies through the functional layer. However, two main mechanisms based on filaments or 2D interfacial effects must be discriminated to better understand and control the devices properties.

We investigate here the key role of oxygen in the switching mechanism of LMO-based RRAMs using hard X-ray photoelectron spectroscopy (HAXPES). This technique allows learning about electrochemical reactions involved in the structure with sufficient depth sensitivity. Operando HAXPES was performed at Soleil and SPring-8 to investigate in-situ resistive switching. Measurements were done while biasing the memory with opposite polarities, to reach successively low and high resistance states. In particular, a chemical analysis of the interface between the active electrode and the LMO was done after *Set* and *Reset* operations.

Results show modifications of the oxygen core level spectra. The peak assigned to interfacial LMO shifts as a function of bias voltage, contrary to the bulk LMO component. These results highlight variations in charges concentration at the electrode/LMO interface, as a result of creation/annihilation of interfacial defects, such as oxygen vacancies. Complementary trends regarding La3*d* and Mn3*s*/2*p* spectra will be discussed in terms of oxidation and reduction phenomena, related to variations of the oxygen content at the electrode/LMO interface.

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[2] Pan F, Gao S, Chen C, Song C, Zeng F, Recent progress in resistive random access memories: Materials, switching mechanisms and performance, Mater. Sci. Eng. R 2014,83:1-59.

5:20pm **SA+AS+MI-WeA10 Combining Hard and Soft X-ray Angle-resolved Photoemission to Probe the Bulk Electronic Structure of Engineered Quantum Solids**, ***Alexander Gray,*** Temple University **INVITED**

Angle-resolved photoelectron spectroscopy, or ARPES, is a powerful and well-established experimental technique for probing the momentum-resolved electronic structure of matter. In this talk, I will discuss several promising new directions in this field, which stem from experimental and theoretical studies wherein angle-resolved photoemission is carried out at higher excitation energies, namely in the soft and hard x-ray regimes. I will focus specifically on the recent studies of novel engineered quantum materials and heterostructures, which aim at gaining a clear understanding of the depth-dependent nanoscale evolution of materials' electronic properties at the surface, in the bulk, and across the buried interfaces by using multiple modalities of hard and soft x-ray angle-resolved photoemission both separately and in tandem with each other.

6:00pm **SA+AS+MI-WeA12 Surface/Interface Coupling in Buried Oxide Interfaces**, ***Conan Weiland,*** National Institute of Standards and Technology (NIST); *A.K. Rumaiz,* Brookhaven National Laboratory; *G.E. Sterbinsky,* Argonne National Laboratory; *J.C. Woicik,* National Institute of Standards and Technology (NIST)

Oxide interfaces can host a variety of properties not found in the bulk materials. The interface between LaAlO3 (LAO) and SrTiO3 (STO) is a prototypical example; the interface of these two insulators can show conductivity, ferromagnetism, and even superconductivity. The source of these interface properties is still a matter of debate, with potential explanations including electronic reconstruction due to the polar discontinuity at the interface, chemical intermixing, and oxygen vacancies at either the interface or LAO surface. Hard x-ray photoelectron spectroscopy (HAXPES) is an excellent tool to probe these interfaces due to the enhanced and tunable probe depth afforded by a synchrotron source. We have used a combination of variable kinetic energy HAXPES and ambient pressure soft x-ray photoelectron spectroscopy (AP-XPS) to investigate the interplay between LAO film and surface structure and the LAO/STO interface. We find Al surface enrichment for most LAO films, while AP-XPS shows significant band shifts in the presence of water vapor. The role of these LAO surface features on the LAO/STO interface conductivity will be discussed.

Surface Science Division

Room 203C - Session SS+AS+EM-WeA

Semiconducting Surfaces

Moderators: Melissa Hines, Cornell University, Ludo Juurlink, Leiden University

2:20pm **SS+AS+EM-WeA1 Functionalizing Semiconductor Surfaces and Interfaces**, ***Stacey Bent,*** Stanford University **INVITED**

Semiconductor surface and interface science serves as the foundation for applications ranging from microelectronics to optoelectronics to bio-sensing. Given the importance of semiconductor surface chemistry in important technologies of today, understanding the fundamental chemistry at a molecular level is key to future advances. This talk will describe studies on the adsorption of organic molecules at semiconductor surfaces, aimed at the ultimate goal of controlling the chemical and electrical properties of these hybrid systems. The presentation will examine model systems of molecular adsorption on the Ge(100)-2×1 surface using a combination of experimental and theoretical methods. The reactivity of different functional groups will be described, with particular focus on reactions of bi- and trifunctional molecules. The results help elucidate the way in which the molecular structure as well as the identity of the reactive moieties affect the product distribution of the molecules upon adsorption. Monolayer surface chemistry is also extended to the formation of covalently-bound organic multilayers through the process of molecular layer deposition (MLD). Results will be presented of our studies to understand MLD mechanisms and bonding. We show that chain termination events during MLD can be counteracted by absorption of precursors into the MLD film, which reintroduces reactive sites that lead to continuation of film growth. We will also describe new MLD chemistries, including photo-initiated MLD that forms new carbon-carbon bonds at the surface.

3:00pm **SS+AS+EM-WeA3 Atomic Structure of UHV-prepared GaP(111)A Surface and its Reactivity Towards Simple Molecules**, ***Denis Potapenko,*** *X. Yang, B.E. Koel,* Princeton University

Effective pyridine-catalyzed photo-reduction of CO_2 to methanol has been demonstrated on p-type GaP(111)A photocathode. Despite the considerable effort there is still no consensus about either the molecular mechanisms of this process or the role of electrode's surface. As a part of larger effort aimed at elucidation of the mechanisms of CO_2 photoreduction we have conducted a UHV study of the atomic-scale structure and reactivity of the single-crystal GaP(111)A surface. Atomic-resolution STM images supported by LEED data show that ion sputtered and annealed surface exhibit both 2 x 2 Ga-vacancy reconstruction and relatively disordered P-trimer formations. The stoichiometric excess of Ga leads to formation of large droplets on the surface. TPD experiments and IR spectroscopy with water and methanol demonstrate dissociative adsorption of these molecules that leads to recombinative desorption around 300 K.

3:20pm **SS+AS+EM-WeA4 Stabilization Mechanism of the Se- or S-treated GaAs(111)B Surface**, ***Shunji Goto,*** The University of Electro-Communications (UEC-Tokyo), Japan; *A. Ohtake,* National Institute for Materials Science (NIMS), Japan; *J.N. Nakamura,* The University of Electro-Communications (UEC-Tokyo), Japan

GaAs surfaces are stabilized by surface treatments with S or Se because of the reduction of the dangling bond density [1,2]. Recently, it has been reported that when the GaAs(111)B-(2 x 2) As trimer surface is treated with Se, the diffraction pattern changes from (2 x 2) to (1 x 1) [3]. The Se-treated GaAs(111)B-(1 x 1) surface was considered to have a simple structure; all As atoms of the ideal (111)B surface are replaced by Se atoms. However, a scanning tunneling microscope (STM) image shows highly disordered array of bright features with a density of 0.25 per (2 x 2) unit [4,5]. This is incompatible with the simple structure model for (1 x 1). Very recently, another structure model has been proposed for the Se-treated surface, where three As atoms on the topmost surface are replaced by Se atoms per (2 x 2) unit. This As / Se terminated model is electronically stable because the so-called electron counting rule is satisfied and the STM simulations for this model reproduces the most of features of STM experiments. In this study, we discuss the structural stability of the As / Se termination model from the viewpoint of the formation energy. We depict a phase diagram as functions of chemical potentials of Se (μ(Se)) and As (μ(As)) using the first-principles calculations within the density functional theory.

Under the As-rich and Se-poor conditions, the (2 x 2) As-trimer surface is the most stable phase. The As / Se terminated surface appears in the phase diagram under more As (Se) poor (rich) conditions, being consistent with the recent experiment [5]. It is noted that the fully-Se-terminated (1 x 1) surface can exist as a stable phase in the limit of Se-rich condition, whereas this surface does not satisfy the electron counting rule and has a metallic surface state attributed to surplus electrons of Se. At the fully-Se-terminated surface, a lone pair forms at each Se site and resultant excess electrons occupy the anti-bonding orbital of the outermost bilayer. As a result, the surface Se atoms hardly leave any dangling bond. We have also found that the S-treated surface is passivated by a similar mechanism.

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4:20pm **SS+AS+EM-WeA7 Novel Pathways in Reaching Buried Interfaces of Organic/Inorganic Hybrid Systems: A Mechanistic Understanding of Polymer Adsorption on Passivated Metal Oxide Surfaces***, **Tom Hauffman**, S. Pletincx, K. Marcoen, F. Cavezza,* Vrije Universiteit Brussel, Belgium*; L.-L. Fockaert, J.M.C. Mol,* Technical University Delft, Netherlands*; H. Terryn,* Vrije Universiteit Brussel, Belgium

The interface between a metal oxide and its coating is of great importance for the durability and efficiency of the entire organic/inorganic hybrid system. However, the analysis of such solid/solid interfaces is challenging, as they are masked by a µm-thick polymer layer on one side and a thick metal oxide matrix on the other side. The main difficulty will be to investigate buried interfaces non-destructively with conventional surface analysis techniques.[1,2]

In this work, we characterize interfacial interactions of several ultrathin polymeric films with aluminum and zinc oxides by utilizing novel methodologies, leading to the characterization of a realistic model interface. The adsorption mechanisms are established by using XPS for chemical state information and ToF-SIMS for direct molecular information of these ultrathin organic overlayers.

The use of these nanometer thin films opens up the possibility of an in situ characterization of environmental influences such as water ingress. The use of Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) is employed to describe the adsorption mechanism in the presence of water vapor. Furthermore, ATR-FTIR Kretschmann is utilized to obtain a near-interface infrared spectrum while simultaneously, the influence of an above-the-polymer electrolyte (such as water) on the interface is characterized.[3]

The homogeneity of these interfacial interactions is characterized on the nanoscale using nano-infrared spectroscopy. This novel technique allows to conduct infrared spectroscopy on the nanoscale by using an AFM tip, which probes the expansion of the material due to IR absorbance. This results in a local vibrational spectrum.

This work comprises novel synthesis routes and methodologies, which enable to probe interfacial changes in hybrid systems non-destructively and in situ. As such, coatings systems can be optimized with respect to the bare substrate.

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4:40pm **SS+AS+EM-WeA8 Surface Modification of Metal Oxide Surfaces with Gas-Phase Propiolic Acid for Dye Sensitization by Click Reaction***, **Chuan He**, A.V. Teplyakov, B. Abraham, M. Konh, Z. Li, L. Gundlach, S. Bai,* University of Delaware*; E. Galoppini, H. Fan, R. Harmer,* Rutgers, the State University of New Jersey

The dye sensitization on metal oxide (ZnO, TiO_2, Fe_2O_3, CuO) surfaces has attracted plenteous attention due to their numerous applications in solar energy conversion, photo-catalysis, sensing, etc. Substantial research efforts focused on designing different dyes and surface nanostructuring. However, the actual chemical attachment schemes still heavily rely on the use of sensitizer molecules functionalized with carboxylic (COOH) or phosphonic ($P(O)(OH)_2$) anchor groups. Despite consequential progress in chemical modification schemes, the very nature of these functional groups may cause very pronounced surface morphology change of the nanomaterials designed because of etching process in liquid phase. In addition, these acidic groups often lead to the formation of multiple binding configurations (such as monodentate or bidentate miixtures) on the surface. To address both issues, we developed a two-step preparation procedure to achieve the morphology preservation of metal oxide surfaces and well-defined covalent binding of the intersurface functionality. The first step requires exposing clean metal oxide nanostructures to a gas-phase prop-2-ynoic acid (propiolic acid) in medium or high vacuum, which results in the formation of a robust and stable surface-bound carboxylate with ethynyl groups available for further modification. For the second step, we applied copper catalyzed click reaction on this preserved surface to covalently bind dye molecules functionalized with azido groups to these pre-functionalized surfaces. For example, a suitable organic dye (9-(4-azidophenyl)-2,5-di-tert-butylperylene (DTBPe-Ph-N_3)) was used to investigate a distinct signature of covalently-bound dye molecules on ZnO nanorods surface. In this study, we have confirmed the morphology preservation and selective covalent attachment of the carboxylic acid onto the metal oxide surface by the combination of measurements including scanning electron microscopy (SEM), infrared, X-ray absorption photoelectron spectroscopy (XPS), solid-state 13C NMR, transient absorption spectroscopy (TA) and density functional theory (DFT) calculations.

5:00pm **SS+AS+EM-WeA9 Solar Energy Storage in the Norbornadiene-quadricyclane System: From Surface Science to In-situ Photochemistry and photospectroelectrochemistry***, M. Schwarz, F. Waidhas, C. Schuschke,* Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*; S. Mohr,* Friedrich-Alexander-Universität Erlangen-Nürnberg*; O. Brummel, T. Döpper, C. Weiss, K. Civale,* Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*; M. Jevric,* Chalmers University of Technology, Gothenburg, Sweden*; J. Bachmann,* Friedrich-Alexander-Universität Erlangen-Nürnberg. Germany*; A. Görling, A. Hirsch,* Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*; K. Moth-Poulsen,* Chalmers University of Technology, Gothenburg, Sweden*; **Jörg Libuda**,* Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany

Photochemical isomerization of small organic molecules enables chemical energy storage via a single-photon-single-molecule process. A prototypical example is the conversion of norbornadiene (NBD) to its strained metastable valence isomer quadricyclane (QC), which releases up to 100 kJ/mol upon cycloreversion. This makes the NBD-QC system a solar fuel with an energy density comparable to state-of-the-art batteries.

In order to obtain a better understanding of NBD-based energy storage systems, we studied both the photochemical conversion and the catalytically and electrochemically triggered back-conversion at atomically defined interfaces. We combined vibrational spectroscopy with in-situ photochemistry in ultrahigh vacuum (UHV) and in electrochemical (EC) environments. In UHV, NBD and QC films were grown by physical vapor deposition (PVD) on Pt(111). By infrared refection absorption spectroscopy (IRAS), we observe spontaneous cycloreversion in QC monolayers even at 130 K, while QC multilayers are stable. Adsorbed NBD adopts a η_2:η_1 geometry which involves an agostic C-H-Pt interaction. At 300 K, this species undergoes dehydrogenation by splitting off the agostic H.

In UHV environments, the conversion from NBD to QC can be triggered in-situ by UV light and a co-deposited photosensitizer (PS). In electrochemical environments, back-conversion can be triggered by the electrode. On Pt(111) electrodes, we monitored the back-conversion in-situ by electrochemical infrared reflection absorption spectroscopy (EC-IRRAS). The corresponding spectra were analyzed based on simulated spectra from density functional theory (DFT). Using a new photoelectrochemical IRRAS setup (PEC-IRRAS), we monitored the complete storage and release cycle by in-situ vibrational spectroscopy. Selectivities were determined both for the conversion and the back-conversion, showing that the stability of the PS is a critical step in the storage cycle. Much higher reversibility could be obtained using new NBD derivatives which avoid an additional PS.

To better control the energy transfer via the electrode interface, we investigated NBD derivatives anchored via a carboxylic-acid function to atomically defined oxide surfaces. In UHV, dense monolayers of surface-anchored NBD derivatives were prepared by PVD onto Co_3O_4(111) films on Ir(100). The molecules adopt an upright-standing orientation with the NBD units pointing away from the interface. Finally, we explored the behavior of these films in (photo)electrochemical environments.

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5:20pm **SS+AS+EM-WeA10 In-situ Characterization of Photon induced Chemistries in Organotin Clusters with Ambient Pressure XPS***, **J. Trey Diulus**[1], R.T. Frederick,* Oregon State University*; M. Li,* Rutgers, the State University of New Jersey*; D.C. Hutchison, I. Lyubinetsky, L. Árnadóttir, M.R. Olsen,* Oregon State University*; E.L. Garfunkel,* Rutgers, the State University of New Jersey*; M. Nyman,* Oregon State University*; H. Ogasawara,* SLAC National Accelerator Laboratory*; G.S. Herman,* Oregon State University

Solution-based organometallic nanoclusters are unique nanoscale material precursors due to the precise control over their size, shape, and structure. The interaction of photons with these clusters can result in the preferential removal of organic ligands at room temperature. This process leads to a change in solubility, which makes these materials prime candidates for next-generation photoresists for extreme ultraviolet (EUV) nanolithography. In this study, we are investigating the interaction of soft X-ray radiation with organotin based clusters to better understand the transition from organometallic to metal oxide nanoclusters. As a model system we are studying the charge neutral, sodium templated, butyl-tin Keggin (β-$NaSn_{13}$) cluster $[NaO_4(BuSn)_{12}(OH)_3(O)_9(OCH_3)_{12}(Sn(H_2O)_2)]$. For analysis, the β-$NaSn_{13}$ clusters were dissolved in 2-heptanone and spin-coated to form uniform thin films (~20 nm thick). Ambient pressure X-ray photoelectron spectroscopy (AP-XPS) was used to measure the Sn 3d, O 1s, and C 1s core-levels, using photon energies above and below key absorption edges. These measurements allowed us to characterize changes in the both the atomic concentrations and chemical states of β-$NaSn_{13}$ under a range of ambient conditions, including ultrahigh vacuum and multiple partial pressures (between 0.01 to 1 Torr) of oxygen, water, methanol, nitrogen, and hydrogen. Successive C 1s scans were collected during exposure to measure the change in intensity with respect to exposure time, ambient, and photon energy. A significant reduction in the C 1s signal was observed for oxygen ambients, suggesting the oxygen partial pressure was able to increase the rate of butyl group desorption from the β-$NaSn_{13}$ clusters. Furthermore, a photon dose array was collected in each condition to determine whether ambient conditions have an effect on the photon induced chemistries leading to a solubility transition. The dose array was plotted as contrast curves, which indicate that an oxygen ambient significantly lowers the required photon dose relative to UHV. We also found that a water ambient significantly increases the required photon dose compared to an oxygen or UHV ambient. These studies ultimately improve the understanding of photon induced chemistries in the β-$NaSn_{13}$ based thin films and provide mechanistic insights for the formation of tin oxide nanomaterials at surfaces.

5:40pm **SS+AS+EM-WeA11 Integrated Photonics Driven Electron Emission from LaB_6 Nanoparticles***, **Fatemeh Rezaeifar**, R. Kapadia,* University of Southern California

In this report, we demonstrate the novel approach of integrated photonics waveguide driven electron emission from Lanthanum hexaboride (LaB_6) nanoparticles drop-casted over the surface of an optical waveguide. We use integrated waveguide under LaB_6 electron emitter as a mean to transport photons and evanescently couple them to emitter. This evanescent coupling occurs through longer interaction length and photons can be absorbed efficiently compared to free space laser illumination from top on a metallic emitter. Furthermore, nanoparticles with the average diameter of 4 nm are at the order of electron mean free path and electron emission occurs with fewer scattering compared to electron emission from conventional bulky metallic emitters. As such, in our proposed device, the higher optical absorption along with fewer scattering inside nanoparticles enable us with larger quantum efficiency electron emitters beyond the available photon driven emitters.

We experimentally studied the photon driven electron emission characteristics obtained by coupling of CW laser (wavelength = 405 nm) to LaB_6 nanoparticle emitters drop-casted on top surface of the silicon nitride (Si_3N_4) integrated waveguide with height of 5 µm and width of 50 µm. Optical V-groove was fabricated for coupling 405 nm laser from 200 µm optical fiber in to Si_3N_4 waveguide. The work function of the LaB_6 is only 2.69 eV and it requires very small E-field to collect the photon driven emitted electrons. We observed photocurrent at E-field as small as 0.3 V/µm while the dark current detection from LaB_6 nanoparticles begins at higher E-field, 3.5 V/µm. In addition, we present the photocurrent dependency on the laser power. At small E-field in which no tunneling is possible, we observed a linear relation between the photocurrent and laser power indicating single photon ability for this emission process. This matches to the expected slope of 1 for single photon absorption process, given that the work function of LaB_6 is only 2.69 eV, and our photon energy at 405 nm is 3.1 eV. Finally, we present the comparative results for the emission properties from LaB_6 nanoparticles illuminated with free space laser to evaluate the performance of the proposed integrated photonics driven emitters. While free space illuminated method results in emission current as small as 1 pA with 390 mW of laser power, the integrated photonics driven emitter emits above 50 pA with much smaller laser power transporting inside the optical waveguide, 100 µW. As such, we conclude integrated photonics driven emitter as a potential solution for increasing the quantum efficiency of the future electron emitters.

6:00pm **SS+AS+EM-WeA12 Photon Stimulated Desorption and Diffusion of CO on TiO_2(110)***, **Nikolay Petrik**, R. Mu, A. Dahal, Z.-T. Wang, Z. Dohnalek, I. Lyubinetsky, G.A. Kimmel,* Pacific Northwest National Laboratory

Thermal diffusion of CO adsorbed on rutile TiO_2(110) was studied in the 20 - 110 K range using photon-stimulated desorption (PSD), temperature programmed desorption (TPD) and scanning tunneling microscopy. During UV irradiation, CO desorbs from certain photoactive sites (e.g. oxygen vacancies). This phenomenon was exploited to study CO thermal diffusion in three steps: first empty these sites during a first irradiation cycle, then replenish them with CO during annealing, and finally probe the active site occupancy in the second PSD cycle. The PSD and TPD experiments show that the CO diffusion rate correlates with the CO adsorption energy – stronger binding corresponds to slower diffusion. Increasing the CO coverage or hydroxylation of the surface decreases the CO binding and increases the CO diffusion rate. Relative to the reduced surface, the CO adsorption energy increases and the diffusion decreases on the oxidized surface. The CO diffusion kinetics can be modeled satisfactorily as an Arrhenius process with a “normal” prefactor (i.e. $\nu = 10^{12}\ s^{-1}$) and a Gaussian distribution of activation energies where the peak of the distribution is ~0.28 eV and the full width at half maximum (FWHM) is ~0.1 eV at the lowest coverages. The observations are consistent with a significant electrostatic component of the CO binding energy on the TiO_2(110) surface which is affected by changes in the surface dipole and dipole-dipole interactions.

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[1] **Morton S. Traum Award Finalist**

Actinides and Rare Earths Focus Topic
Room 202C - Session AC+AS+SA-ThM

Nuclear Power, Forensics, and Other Applications

Moderator: Ladislav Havela, Charles University, Prague, Czech Republic

8:00am **AC+AS+SA-ThM1 Electron Microscopy in Nuclear Forensics*, Edgar Buck*,** *D.R. Reilly, J.M. Schwantes, J.A. Soltis, T.Q. Meadows, D.A. Meier, J.F. Corbey,* Pacific Northwest National Laboratory **INVITED**

Recent advances in electron microscopy both in terms of spatial resolution, sensitivity, and the ability to perform in-situ chemistry experiments, present enormous opportunities to the nuclear forensic field. Extraction of specific particles of interest with dual-beam SEM-FIB instruments can be readily applied plutonium-contaminated materials. Furthermore, other developments in microscopy have enabled in-situ monitoring of interfacial processes and 3D tomographic views of specimens and phases. Several new advances in technology have enabled great advances and potential for nuclear science including nuclear forensics. These include dual-beam ion-electron systems for precise sample isolation and preparation, the electromagnetic lens aberration-corrector, high-count capacity x-ray detector systems, faster digital cameras, high performance electron backscattered diffraction systems in combination with 3D visualization tools, application of cryoTEM methods to material science, as well as micro-fabricated in-situ cells that enable direct observation of chemical and electrochemical processes in the EM. The application of these technologies to nuclear forensics will be discussed.

8:40am **AC+AS+SA-ThM3 New Frontiers with Fission Track Analysis and TOF-SIMS Techniques*, Itzhak Halevy,*** Nrcn Israel*; R. Radus,* Ben Gurion University, Israel*; S. Maskova,* Charles University, Prague, Czech Republic*; A. Kogan, S. Samuha, D. Gridchin, E. Grinberg, E. Boblil, N. Haikin,* IAEC-NRCN, Israel*; I. Orion,* Ben-Gurion University -Negev, Israel*; A. Weiss,* Faculty of Engineering, Bar-Ilan University, Israel **INVITED**

Illicit trafficking of radioactive materials is known to exist from the early days of radioactive era. The nuclear forensics deals with recognizing the materials and processes of the radioactive industry. The properties of the materials can give a hint about the source of material and its original use.

The most common radioactive material involved in illicit trafficking is uranium. Uranium is a common natural element which can be found everywhere. The cosmogenic uranium is well known and defined. The natural enrichment of uranium is varying within a small range around 0.72 % and is indicative to its source. The enrichment of the anthropogenic uranium can vary much depending on the purpose and use of the material. Different enrichments are known for individual nuclear power plants, research reactors and military uses.

Measuring the uranium properties can indicate its enrichment, presence of other elements or impurities and can help in finding its attribution, namely its origin.

To learn more about the history of found material accurate isotopic measurements are needed.

The ratio between ^{230}Th and ^{234}U can give a good estimation of how much time passed from the last chemical cleaning of the material. This technique is called radio-chronometry or age dating.

We developed new Lexan detectors with much better signal to noise ratio to improve sensitivity and reduce the false alarm.

New Automated software can recognize the fission track (FT) automatically and give the parameters of the track, like: roundness, intensity, number of tracks and color histogram. In that program we can add ROI (region of interest) or to cancel a false positive FT identification.

Analytical equipment like TOF-SIMS (Time Of Flight - Secondary Ion Mass Spectrometry) and ICP-MS (Inductively Coupled Plasma - Mass Spectrometer located at the Geophysical survey Israel - GSI) together with new FTA software give new frontiers to the nuclear forensic research .

A microscope equipped with TOF-SIMS gives the ability to measure quantitatively, the ratio between the different isotopes and molecules. Using the scanning electron microscope, we are able to choose the desired particle which can be then analyzed using the TOF-SIMS. TOF-SIMS is a technique capable to distinguish not only between elements but also different isotopes. Knowing the ratio between the isotopes is very important as it can help us to classify the material looking for its possible origin. Morphology and depth profile than give other insight to the processes that the sample went through. Nano manipulators can extract the particle and transfer it to a different technique.

9:20am **AC+AS+SA-ThM5 Predictive Nuclear Forensics: Fundamental Frameworks to Fill Missing Pieces*, Jenifer Shafer*,** *M. Koehl, A. Baldwin, D. Wu,* Colorado School of Mines*; R. Rundberg,* Los Alamos National Laboratory*; M. Servis,* Washington State University*; T. Kawano,* Los Alamos National Laboratory **INVITED**

Understanding the origin of nuclear forensic signatures provides the benefit of understanding how these signatures can be compromised and provides a framework to predict signatures that might arise under various conditions. The ability to predict signatures is particularly useful for the nuclear forensics community since only a limited number of samples exist. Frequently access to these samples can be further constrained due to classification boundaries. This talk provides two examples of how fundamental chemical and physical phenomena can be leveraged to understand signature origins, thus enabling a more robust nuclear forensics capability. The first study focuses on understanding how organic phase aggregation chemistry in the PUREX process can dictate trace metal, such as fission or corrosion product, partitioning patterns. By understanding how trace metals partition, information regarding the processing history, including the reprocessing site, could be ascertained. Trace metal partitioning patterns were studied by producing radiotracers in the USGS 1 MW TRIGA reactor. The influence of extractant aggregation on trace metal partitioning was then assessed using a combination of diffusion NMR spectroscopy and small angle neutron scattering. The second study focuses on understanding how cumulative fission product yields can describe the incident neutron energy. Fission yield curves of uranium-235 have a decrease in valley radionuclide production when the incident neutron energy is in the epithermal energy regime. This decrease in valley radionuclide production seems tied to the excitation of the uranium-236 to the 3- spin state. The octopule deformation of the 3- spin state enables more asymmetric fission than typically encountered with fast or thermal neutrons and thus suggests the structure of the excited uranium-236 compound nucleus could be, in part, responsible for cumulative fission product yields. These two studies highlight how fundmental science enables signature development.

11:00am **AC+AS+SA-ThM10 Soft X-ray Synchrotron Radiation Spectromicroscopy Studies of Radioactive Materials*, David Shuh*,** Lawrence Berkeley National Laboratory*; A. Altman,* Lawrence Berkeley National Laboratory and UC Berkeley*; A.L.D. Kilcoyne, S.G. Minasian, J.I. Pacold, D.E. Smiles, T. Tyliszczak, D. Vine,* Lawrence Berkeley National Laboratory*; L. He, J. Harp, M. Meyer,* Idaho National Laboratory*; C. Degueldre,* University of Lancaster, Switzerland

Soft X-ray synchrotron radiation methodologies are being developed and employed at the Advanced Light Source (ALS) of Lawrence Berkeley National Laboratory (LBNL) to elucidate the electronic structure of radioactive and actinide materials. Results from these investigations have begun to provide improved fundamental knowledge that can be used as a scientific basis for the enhanced design of actinide materials, complexes, ligands, and the overall understanding of actinide materials. The experimental developments at the ALS have centered on studies of radioactive materials with the soft X-ray scanning transmission X-ray microscope (STXM) at Beamline 11.0.2 for spatially-resolved near-edge X-ray absorption spectroscopy (XAS). The spectromicroscopy capabilities of the STXM provide the means to determine the speciation and composition in a range of actinide materials, particularly those of technological and environmental interest with spatial resolution that can reach to the true nanoscale. A particular emphasis has been on the use of light atom (B, C, N, O, F, Na, Mg, Al, Si) ligand K–edge XAS technique to determine the electronic structure characteristics in an array of unique and relevant materials. Furthermore, there are a host of additional electron energy level thresholds (such as the L–edges of the transition metals, the M–edges of the lanthanides, and others) that can be probed by near-edge XAS in the soft X-rays.

Recently, STXM spectromicroscopy studies have been extended to focused ion beam (FIB) prepared radioactive and irradiated material specimens in collaboration with Idaho National Laboratory. Future scientific developments and applications of soft X-ray spectromicroscopy investigations utilizing ptychography and in-operando methodologies will be discussed.

11:20am **AC+AS+SA-ThM11 Comparison of the Oxidation Rates for Alpha Versus Delta Plutonium by X-ray Photoelectron Spectroscopy*, Art Nelson,*** *S.B. Donald, D.J. Roberts, W. McLean,* Lawrence Livermore National Laboratory

X-ray photoemission spectroscopy (XPS) was used to characterize differences in the oxidation rates for polycrystalline α-Pu versus δ-Pu related to variations in grain size and surface electronic structure. The evolution of the Pu 4f core-level chemical shift as a function of oxygen exposure at ambient temperature was quantified in oxidation profiles. In addition, the X-ray excited Pu NOO Auger line-shapes were combined with the chemical shift of the Pu $4f_{7/2}$ photoelectron line that defines the Auger parameter and results in a reliable method for determining oxidation states independent of binding energy calibration. The oxidation profiles reveal that α-Pu oxidizes faster than δ-Pu, both resulting in the $PuO_2/Pu_2O_3/Pu$ oxide structure. This data was used to a produce chemical state (Wagner) plot for select plutonium oxides.

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

11:40am **AC+AS+SA-ThM12 A Single-Stage AMS Detector for Secondary Ion Mass Spectrometry and its Applications to Nuclear Materials Analyses*, David Willingham,*** *E.E. Groopman, K.S. Grabowski,* U.S. Naval Research Laboratory*; L. Sangely,* International Atomic Energy Agency*; A.P. Meshik, O.V. Pravdivtseva,* Washington University in St. Louis*; D.G. Weisz, K.B. Knight,* Lawrence Livermore National Laboratory

Secondary ion mass spectrometry (SIMS) has long been applied to the analysis of isotopic heterogeneities in nuclear materials. Few other methodologies can compete with the ability of SIMS to measure the isotopic composition of nuclear materials with high accuracy and precision with micrometer spatial resolution. Like many other mass spectrometry techniques, however, the presence of molecular isobaric interferences at any given mass-to-charge complicate interpretation of SIMS measurements. Uranium isotopes, for example, can be valuable and informative markers for the process of enriching uranium for nuclear fuel for the production of nuclear energy. In addition to the major uranium isotopes (^{238}U and ^{235}U), the minor isotope ^{236}U is of interest because it is an indication for the presence in the sample of uranium reprocessed from spent nuclear fuel. The resolving power needed to separate ^{236}U from the molecule $^{235}U^1H$, however, is greater than 38,000 - far beyond most the mass resolution of commercially available SIMS instruments. One solution to this problem is to use a Single-Stage Accelerator Mass Spectrometer (SSAMS) to accelerate secondary ions to a high enough energy (300keV) to enable molecular dissociation within a stripper gas while retaining good transmission, followed by SIMS-based detection. At the U.S. Naval Research Laboratory, we have developed the Naval Ultra-Trace Isotope Laboratory's Universal Spectrometer (NAUTILUS) to achieve this goal. Using the NAUTILUS, we accomplish molecule-free isotopic analysis of nuclear materials without sacrificing the benefits of SIMS. In this work, we demonstrate the broad applications of the NAUTILUS to areas of nuclear materials analyses including uranium bearing particle analysis for nuclear Safeguards, analysis of the Oklo natural nuclear reactor, and analysis of uranium doped silicate glasses as working reference analogs for nuclear fallout materials. The NAUTILUS represents a new era in SIMS analyses of complex materials with specific application to nuclear materials and general application to the SIMS community as a whole.

12:00pm **AC+AS+SA-ThM13 Physicochemical Properties of Ag in Annealed ZrN/SiC/Ag Heterostructures Used to Simulate TRISO Nuclear Fuels*, Jeff Terry,*** *M. Warren, R. Seibert,* Illinois Institute of Technology

Silicon carbide (SiC) is used as a supportive and protective barrier in the cladding of tristructural-isotropic (TRISO) nuclear fuel particles. Previous studies both of surrogate surfaces and irradiated fuel have shown that the fission product silver (Ag) exhibits transport into and sometimes through the SiC barrier with temperatures above 500 °C. This silver release can cause safety concerns for maintenance workers due to plate-out on in-reactor components. Although an exact diffusion mechanism for Ag in SiC is unknown, a solution is needed to prevent this effect. The use of a ZrN protective coating may mitigate Ag transport and potential release. This study examines the transport of Ag in SiC through the use of surrogate multilayered thin-films. Thin films of subsequent layers of SiC, Ag, SiC, and ZrN deposited by pulsed-laser ablation deposition (PLD) under a range of annealing temperatures up to 1200 °C are studied. After heating, X-ray photoemission spectroscopy (XPS), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS) was used to examine the surface of the ZrN. Initial results show that Ag does not readily diffuse through the ZrN layer like it does through SiC. The results and implications of this study will be discussed.

Applied Surface Science Division
Room 204 - Session AS+SE-ThM

Applied Surface Analysis of Novel, Complex or Challenging Materials

Moderators: Michael Brumbach, Sandia National Laboratories, Thomas Grehl, IONTOF GmbH, Germany

8:00am **AS+SE-ThM1 Understanding the Surface of Complex Oxides used in High Temperature Electrochemical Devices*, John Kilner,*** Imperial College London, UK*; J.W. Druce,* International Institute for Carbon Neutral Energy Research (I2CNER), Japan*; H. Tellez, A. Staykov,* International Institute for Carbon Neutral Energy Research (I2CNER) **INVITED**

High temperature electrochemical devices, such as solid oxide fuel cells and electrolyzers, have been under development for application in clean energy systems for many years. Although acceptable performance can be achieved, the requirements of low cost and high durability have been a major hurdle to commercialization. This has necessitated a lowering of the operating temperature from circa 800-900ºC, to temperatures in the region of 500-600ºC, with a consequent loss of electrochemical activity of the electrodes, particularly the air electrode. Key to optimizing performance is gaining an understanding of the gas/solid interface between the Mixed Ionic Electronic Conducting (MIEC) electrodes and the oxygen-rich ambient, and how the structure, composition and activity evolves with time. We have used a multifaceted approach to probe the surfaces of ceramic mixed conductors, after treatment in typical SOFC cathode operating conditions. This has involved ion beam based techniques such as Low Energy Ion Scattering (LEIS) to sample the composition of the outermost atomic layers of ceramic materials, Secondary Ion Mass Spectrometry (SIMS) to measure oxygen exchange activity, complemented by Density Functional Theory (DFT) to clarify possible mechanisms.

The surface termination of substituted $(AA')(BB')O_3$perovskite-based MIEC materials, such as $La_{1-x}Sr_xCo_{1-y}Fe_yO3\text{-}\delta$ (LSCF), has been studied using LEIS [1] and shown to be dominated by A cations and oxygen, and in particular by segregation of the Sr substituent. For selected $(AA')(BB')O_3$ compositions, we have investigated the rate of oxygen exchange and shown changes in surface activity that are related to changes in surface chemistry. We have used the knowledge gained from experiment to guide theoretical investigations, to aid in the optimization of candidate air electrode materials. This theoretical study was performed using DFT to simulate the interaction of an oxygen molecule with representative AO and A'O segregated surfaces [2,3].

This combination of theoretical studies guided by advanced surface analysis techniques (i.e. LEIS and SIMS) is enhancing our understanding of processes which determine the performance of these important clean energy devices.

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8:40am **AS+SE-ThM3 Vectorial Method used to Monitor a XPS Evolving System: Titanium Oxide Thin Films under UV Illumination***, S. Bechu,* Institut Photovoltaïque d'Ile-de-France*; N. Fairley,* Casa Software Ltd, UK*; L. Brohan,* Institut des materiaux Jean Rouxel, France*; **Vincent Fernandez,*** Université de Nantes, Institut des matériaux Jean Rouxel, France*; M. Richard-Plouet,* Institut des matériaux Jean Rouxel, France

1. Introduction

Third generation solar cells aims at increasing efficiency to overtake the 31% theoretical efficiency of simple junction photovoltaic cells established by Shockley and Queisser . According to Marti and Luque [1] , intermediate band cell concept could increase the photocurrent via the absorption of sub-bandgap photons without degrading the voltage. In this perspective, we developed hybrid photosensitive sols-gels based on titanium complexes with specific optical and electronic properties [2] . Once illuminated under UV light, an intermediate band (IB) appears in the band structure so the absorption spreads over visible to near infrared due to reduction of Ti(IV) in Ti(III) [3] and leads to several important changes in the titanium oxide based nanomaterial chemistry. Thanks to this absorption range increase, these gels could be used as active layers in solar cells.

2. Analysis applied to characterize chemical modifications

In order to get insight in the chemical modifications induced by the creation of the IB, XPS experiments were conducted on thin films while UV illumination was performed *in situ*. We present here a new mathematical method which can be applied to XPS measurements when an evolving set of data is recorded: the vectorial method [4,5]. In this case this method is applied simultaneously to Ti 2p and O 1s XPS peaks [6]. From the data set analysis, we established that each of the two Ti(IV) and Ti(III) signals can be split into two components: one Ti(IV) at 458.4 eV is associated to one Ti(III) at 457.1 eV whereas, under UV illumination, a second Ti(IV) peak appears and evolves similarly than a second Ti(III) peak, at 458.1 and 456.7 eV respectively. Those features were obtained from the vectorial method. It was successfully applied to *in situ* UV illumination allowing to get the percentage of thin films photoreduction, the chemical state appearing upon illumination and evolution.

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9:00am **AS+SE-ThM4 XPS Characterization of Copper and Silver Nanostructures*, Tatyana Bendikov*, *M.D. Susman, F. Muench, A. Vaskevich, I. Rubinstein,* Weizmann Institute of Science, Israel

X-ray Photoelectron Spectroscopy (XPS) is uniquely suited for the direct characterization of nanomaterials in terms of elemental composition, chemical and electronic states of the elements and thin layer thicknesses. Here we present examples where XPS analysis provides critical information for understanding the growth and oxidation mechanisms of metal nanostructures.

Studies of solid-state oxidation of copper nanoparticles (NP) by in-situ plasmon spectroscopy complemented by electron microscopies showed formation of oxide/(metal+void) core-shell structure.[1] XPS analysis allows us to unambiguously identify the presence of both CuO and Cu_2O phases in the oxide shell, and to calculate the relative thicknesses of each layer. These data, in combination with electrochemistry, provide proof for a quantitative model of Cu NPs oxidation.

In a recent study, we investigated the mechanism of the electroless formation of nanostructured silver nanoplatelet (NPL) films in the presence of a Fe(III)-tartrate complex.[2] Electron microscopy and XRD showed that NPLs are formed by secondary nucleation on the edges, while nucleation on the flat (111)-oriented faces is suppressed. XPS analysis of NPLs confirmed strong Fe(III)-tartrate adsorption to the Ag NPS surface. XPS studies of the Fe chemical environment reveal the possible formation of polymeric complexes in the adsorbed layer, which may explain the almost complete inhibition of secondary nucleation on the flat (111) surfaces of Ag NPLs.

References:

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[*]Prof. Israel Rubinstein deceased on October 21, 2017.

9:20am **AS+SE-ThM5 Quantification of Hydroxyl, Major Element and Trace Element Concentrations in Oxide Glasses by Quadrupole SIMS.*, Albert Fahey*, *A.R. Sarafian, T. Dimond,* Corning Inc.

Major and trace element calibrations have been established for positive and negative secondary ions measured by Quadrupole SIMS. A Cs+ primary ion beam is used exclusively and element secondary ions are measured directly, not by the MCs+ method. This affords greater sensitivity and is better matched to the operating characteristics of a quadrupole mass spectrometer than by using MCs+ for positive ion species only. Both natural well-studied geologic glasses and Corning research glasses that have been thoroughly characterized have been used to establish the calibrations.

The CAMECA 4550 Quadrupole SIMS is well-suited to measurement of oxide glasses. Charge-compensation is easily achieved for a Cs+ primary beam on uncoated samples of almost any size. This allows the measurement of concentration of species in the surface of glass (from a few nanometers to several micrometers) that can have a significant impact on the physical and chemical durability of the glass. Because oxide glasses contain oxygen as their major element both positive and negative ions can be generated by sputtering with Cs. Although the use of a Cs primary ion beam is generally associated with measurement of negative secondary ions or the use of MCs+ secondary ions, the presence of oxygen in the glass allows production of a significant quantity of positive ions yielding linear calibrations for species that typically would produce positive secondary ions with an oxygen primary beam. Of course, secondary negative ions are produced as well and for the appropriate elements and small molecular ions yield linear calibrations as well.

Detection limits and details of the calibrations will be shown and discussed and examples-measurements of near surface composition changes in various oxide glasses will be shown. Connections of surface chemistry to other glass-properties will be made and explained.

9:40am **AS+SE-ThM6 Modification of Sputtered Carbon Surfaces in Biosensor Arrays*, Varun Jain*, *M.R. Linford,* Brigham Young University

We describe the chemical modification of carbon surfaces with an eye towards employing them in biosensor (DNA) arrays. Carbon was deposited in thin film form by DC and HIPIMS magnetron sputtering. These depositions were confirmed by atomic force microscopy step height measurements. As indicated by X-ray photoelectron spectroscopy (XPS), the resulting material contained some oxidized carbon at its surface, including –COOH type moieties. These groups could be directly activated for amine attachment using a combination of a carbodiimide (EDC) and sulfo -N-hydroxysuccinimide. Direct attachment of a variety of amines was then possible on this surface, where this process could be followed through the N 1s XPS signal. The surfaces were also activated by direct chlorination using PCl_5, where this process could again be followed by XPS – XPS revealed the introduction and disappearance of chlorine. That is, the chlorine on the resulting carbon surfaces could be nucleophilically replaced with a variety of amines. The DC and HIPIMS sputtered carbon films showed different numbers of reactive functional groups, and the HIPIMS carbon shows unusually smoothness and density by scanning electron microscopy.

11:00am **AS+SE-ThM10 The Role of Surface Analysis in Characterization of Synthetic Opioids: TOF-SIMS imaging of Fentanyl and Fentanyl Analogs for Forensics and First Responder Safety*, Greg Gillen*, *S. Muramoto, J. Verkouteren, E. Sisco,* National Institute of Standards and Technology (NIST)

The misuse and addiction to opioids including heroin and synthetic opioids such as fentanyl and its various analogs has become a national crisis. Drug overdoses have become the leading cause of death for Americans under the age of 50 with 64,000 overdose related deaths in 2016. The extreme potency of fentanyl and its analogs (100-10,000 times more potent than morphine) may result in even very small doses causing life threatening overdoses. The potency is also a safety concern due to the potential for accidental exposure of law enforcement, first responders, forensic lab personnel and health care providers. To address this concern, several trace chemical analysis techniques are being evaluated as presumptive methods for identification of a suspected opioid while minimizing exposure to end users (1). In addition, since the bulk of illicitly manufactured fentanyl enters the US via overseas mail, there is interest in application of the same chemical screening techniques for detection of fentanyl residues on packages to support interdiction. To facilitate the continued development, evaluation and optimization of the aforementioned screening tools, TOF-SIMS imaging and mass spectral analysis is being used to characterize the particle size and chemical composition of fentanyl and related compounds produced by solution casting of pure materials onto metal substrates or as particles collected on conductive adhesive tapes after sampling the outsides of packages containing suspected opioids. TOF-SIMS was able to image and provide unique mass spectral signatures from individual particles of heroin, fentanyl and several analogs. In order to increase the sensitivity of TOF-SIMS for particle identification, we have evaluated the use of acidic polymer substrates (Nafion) as proton donating particle collection substrates. Preliminary results suggest orders of magnitude improvements in protonated secondary ion signals for fentanyl. Finally, the screening technologies being developed were not designed with consideration of the significant toxicity of fentanyl and fentanyl analogs in the form of respirable aerosols. In a typical screening analysis, thermal desorption from a collection swipe can lead to the formation of aerosols in micrometer size range posing a possible risk of toxic exposure to the analyst. TOF-SIMS was also used to characterize the size distribution of thermally desorbed aerosols emitted by these techniques.

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11:20am **AS+SE-ThM11 3D TOF SIMS, Parallel Imaging MS/MS, and XPS Analysis of Glitterwing (*Chalcopteryx rutilans*) Damselfly Wings***, **Ashley Ellsworth**, D.M. Carr, G.L. Fisher, B.W. Schmidt,* Physical Electronics*; W.W. Valeriano, W.N. Rodrigues,* UFMG, Brazil

The male Amazonian glitterwing (*Chalcopteryx rutilans*) damselfly has transparent anterior wings and brightly colored iridescent posterior wings. The colors are important for damselflies 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 colors span the visible spectrum with red, blue, and yellow/green regions on the wings. 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 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^+. With the recent addition of MS/MS capabilities, a conventional TOF-SIMS (MS1) precursor ion analysis and tandem MS (MS2) product ion analysis of targeted precursor ions may be acquired simultaneously and in parallel. The parallel imaging MS/MS is a powerful tool allowing for unambiguous peak identification and provides the maximum information from a given analytical volume.

Here, we explore the use of MS/MS to characterize the chemical composition of the waxy cuticle present on the outer surface of the damselfly wing. 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. [2] Further, we will compare and contrast XPS large cluster Ar_n^+ depth profiling results to reveal the complementary nature of the two techniques.

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[2] D. M. Carr, A. A. Ellsworth, G. L. Fisher, et al., Characterization of natural photonic crystals in iridescent wings of damselfly Chalcopteryx rutilans by FIB/SEM, TEM, and TOF-SIMS, Biointerphases 13 (2018), 03B406.

11:40am **AS+SE-ThM12 Characterization of Aniline Dyes in the Modern Colored Papers and the Prints of José Posada***, J.K. Hedlund, L.D. Gelb, **Amy Walker**,* University of Texas at Dallas

José Posada was a Mexican artist active during the turn of the 20th century, and is often called the father of modern Mexican printmaking. Many of his prints ("broadsides") have vivid colors but are in urgent need of repair. The dyes that give these broadsides their colors are aniline dyes which are soluble in many solvents. Solvents are often used in paper conservation for the removal of pressure-sensitive tapes, and so treatment protocols that preserve these colors are needed. To develop these methods the aniline dyes need to be identified and characterized.

Dye identification requires either non-destructive *in situ* techniques, such as Raman spectroscopy, or *ex situ* techniques with very high sensitivity; only extremely small samples can be taken in order to preserve the integrity and appearance of the broadsides. Although Raman spectroscopy has been employed to analyze Posada prints it has only limited success especially in the analysis of blue and yellow dyestuffs.

We present a new strategy for analyzing dyed paper samples using secondary ion mass spectrometry (SIMS) and analysis of the resulting data using maximum *a posteriori* (MAP) reconstruction. To test our protocol, we first characterized modern cotton paper colored with a range of aniline dyes. Subsequently we analyzed fiber samples taken from Posada prints. Using SIMS, we are able to identify the dyes used in Posada prints, including hitherto unidentified blue and yellow dyes. Furthermore, MAP analysis provides not only unambiguous identification of the dye adsorbed in the paper by comparison with pure-dye reference samples, but also the characteristic mass spectrum of the paper itself.

12:00pm **AS+SE-ThM13 GaAs and Si Surface Energies derived from Three Liquid Contact Angle Analysis (3LCAA), as a Function of Oxygen Coverage for Heterogeneous Nano-Bonding™***, **Sukesh Ram**,* Arizona State University*; K.L. Kavanagh,* Simon Fraser University, Canada*; F.J. Ark, C.E. Cornejo, T.C. Diaz, M.E. Bertram, S.R. Narayan, J.M. Day, M. Mangus, R.J. Culbertson, N. Herbots,* Arizona State University*; R. Islam,* Cactus Materials, Inc.

Native oxides used as surface passivation during semiconductor processing hinder the formation of high quality epitaxial layers. In this research, the surface energies and oxygen content of native oxides of Si(100) and GaAs(100) are measured before and after surface processing prior to a wafer bonding process at T<220°C, "NanoBonding™" [1,2]. Based on Van Oss's theory, Three Liquid Contact Angle Analysis (3LCAA) yields the total surface energy, y^T, of semiconductors and insulators. Van Oss models y^T as combining of molecular interactions or "Lifshitz-Van der Waals" energy y^{LW} with the energy of interaction with electron donors, y^+,and acceptors, y^-. A new automated image analysis algorithm, "Drop and Reflection Operative Program"(DROP), enables fast, accurate and reproducible extraction of contact angles without subjectivity, reducing to <1° the typical ~5° error between contact angles measurements due to manual extraction. Using for each wafer, a minimum of 12 to 30 drops yields 48 to 120 contact angles, yielding y^T , y^{LW}, y^+ and y^- with accuracies better than 3%. By using Ion Beam Analysis (IBA) combining <111> channeling in (100) crystals with the 3.039 ± 0.01 MeV (^{16}O, ^{16}O) nuclear resonance, oxygen coverage can be measured with ML accuracy before and after processin, via SIMNRA simulations, correlating oxygen coverage to data within 1%.

Boron-doped p^-Si(100) is found to be always hydrophilic pre-etch, with a y^T of 53 ± 1.4 mJ/m^2. After an aqueous HF (1:20) etch, y^T decreases 10% to 48 ± 2.6 mJ/m^2, and Si is hydrophobic. GaAs(100) is initially always very hydrophobic with a y^T of 37 ± 2.0 mJ/m^2. After etching, Te-doped n+GaAs always becomes hydrophilic with a y^T increase of 50% to 66 mJ/m^2 ± 1.4 mJ/m^2. Native oxides on B-doped p^-Si(100) wafers are found by IBA to contain 13.3×10^{15} at/cm^2 or 13.3 ± 0.3 oxygen monolayers (ML). After an aqueous HF (1:20) etch, Si(100) exhibits only a 11.6 ± 3% reduction in oxygen to 11.8 ± 0.4 ML . GaAs native oxides contain 7.2 ± 1.4 oxygen ML. After a proprietary passivation-based etch, GaAs native oxides are reduced 49.1 ± 4% to 3.6 ± 0.2 oxygen ML without change in GaAs surface stoichiometry.

3LCAA can quantify accurately the reactivity of a surface before Nano-Bonding™, which can be correlated to oxygen coverage and structure. High-resolution IBA and 3LCAA allows for a quantitative analysis of Si and GaAs surfaces energies as function of surface processing, enabling for the engineer interactions between surfaces for NanoBonding.

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2. Herbots N., Islam R., US Pat. Pending (2018), filed March 18, 2018

Advanced Ion Microscopy Focus Topic
Room 203B - Session HI+AS-ThM

Advanced Ion Microscopy & Surface Analysis

Moderators: Gregor Hlawacek, Helmholtz Zentrum Dresden-Rossendorf, Germany, Shida Tan, Intel Corporation

8:00am **HI+AS-ThM1 Pushing the Limits: Secondary Ion Mass Spectrometry with Helium Ion Microscopy*, Alex Belianinov*,** Oak Ridge National Laboratory*; S. Kim,* Pusan National University, South Korea*; M. Lorenz,* University of Tennessee Knoxville*; A.V. Ievlev, A. Trofimov, O.S. Ovchinnikova,* Oak Ridge National Laboratory **INVITED**

Material functionality is defined by structure and chemistry often at micro- and nano-scale. The effects are coupled; however, few methods exist that can simultaneously map both. This presents a challenge for material scientists. Functional materials are continuously increasing in complexity, and the number of studies devoted to designing new materials often overwhelms characterization capacity. Recently, attention has been devoted to offer hardware and software solutions in chemical imaging, where a blend of *in-situ* and *ex-situ* techniques are used to capture and describe material behavior using combinatorial data. However, many of the emerging techniques need to be carefully validated and contrasted against existing approaches.

This talk will cover the performance of the recently developed combinatorial Helium Ion Microscopy (HIM) and Secondary Ion Mass Spectrometry (SIMS) tool on a wide variety of conductive and insulating samples. While the HIM imaging and milling performance to explore the physical structure has been repeatedly demonstrated, questions on the effect, quality, and resolution of a Neon beam SIMS remain. Ion yields, chemical resolution, and charge compensation results and strategies will be presented and discussed.

Acknowledgement

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

8:40am **HI+AS-ThM3 When HIM meets SIMS*, Tom Wirtz,*** Luxembourg Institute of Science and Technology (LIST), Luxembourg*; O. De Castro, J. Lovric,* Luxembourg Institute of Science and Technology (LIST)*; J.-N. Audinot,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

In 2015, we first presented a Secondary Ion Mass Spectrometry (SIMS) system which we specifically developed for the Zeiss ORION NanoFab Helium Ion Microscope (HIM) [1]. This SIMS system is based on (i) specifically designed secondary ion extraction optics coupled with post-acceleration transfer optics, providing maximized extraction efficiency while keeping a finely focussed primary ion beam for highest lateral resolution, (ii) a compact floating double focusing magnetic sector mass spectrometer allowing operation in the DC mode at full transmission (and hence avoiding duty cycles like in TOF systems that either lead to very long acquisition times or, for a same acquisition time, intrinsically limit the sensitivity) and (iii) a specific detection system allowing the detection of several masses in parallel. We have demonstrated that our instrument is capable of producing (i) mass spectra with high mass resolution, (ii) very local depth profiles and (iii) elemental SIMS maps with lateral resolutions down to 12 nm [1-5]. Furthermore, HIM-SIMS opens the way for in-situ correlative imaging combining high resolution SE images with elemental and isotopic ratio maps from SIMS [2,3,6]. This approach allows SE images of exactly the same zone analysed with SIMS to be acquired easily and rapidly, followed by a fusion between the SE and SIMS data sets [6]. Moreover, thanks to its depth profiling capability of the SIMS add-on, it is now possible to follow the chemical composition in real time during nano-patterning in the HIM for applications such as end-pointing.

Here, we will review the instrument performance and present a number of examples taken from various fields of applications, with a special emphasis on 3D reconstructions in materials science (battery materials, solar cells, micro-electronics) and on correlative HIM-SIMS bioimaging.

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9:00am **HI+AS-ThM4 Deciphering Chemical Nature of Ferroelastic Twin Domain in MAPbI₃ perovskite by Helium Ion Microscopy Secondary Ion Mass Spectrometry*, Yongtao Liu,*** University of Tennessee*; L. Collins,* Oak Ridge National Laboratory*; R. Proksch,* Asylum Research an Oxford Instruments Company*; S. Kim,* Oak Ridge National Laboratory*; B.R. Watson,* University of Tennessee*; B.L. Doughty,* Oak Ridge National Laboratory*; T.R. Calhoun, M. Ahmadi,* University of Tennessee*; A.V. Ievlev, S. Jesse, S. Retterer, A. Belianinov, K. Xiao, J. Huang, B.G. Sumpter, S.V. Kalinin,* Oak Ridge National Laboratory*; B.H. Hu,* University of Tennessee*; O.S. Ovchinnikova,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

Hybrid organic-inorganic perovskites (HOIPs) have recently attracted attention due to its success in optoelectronics, largely due to power conversion efficiency, which has exceeded 20% in a short time. Recently, the appearance of twin domains in $MAPbI_3$ has been described ambiguously in a number of investigations. While all previous publications are limited in the descriptions of ferroelectric and/or ferroelastic nature, given (i) the correlation of defect chemistry and ferroelasticity, (ii) the coupling of ferroelectricity and ionic states, the chemistry of this twin domain can no longer be ignored. In earlier investigations, the twin domain size is revealed in the range of 100 nm- 400 nm, well in the detectability of helium ion microscopy secondary ion mass spectrometry (HIM-SIMS) (spatial resolution ~10 nm). Therefore, in this work, we correlate HIM-SIMS with multiple image techniques to unveil the chemical nature of the twin domain in $MAPbI_3$ perovskite.

Our scanning probe microscopy (SPM) studies indicate the variation of elasticity and energy dissipation between domains. Moreover, correlating SPM with scanning electron microscope (SEM), we observed smooth topography and twin domain contrast in SEM image, simultaneously, indicating the twinning contrast in SEM image is not due to morphology. These results allow us to suppose the chemical variation between twin domains, suggesting the need of clarifying the chemical difference between domains.

Using HIM-SIMS, which combines high-resolution imaging <0.25 nm of helium ion microscopy with the chemical sensitivity of secondary ion mass spectrometry (SIMS), we can detect ion distribution with a spatial resolution of 10 nm, allowing us to quantitatively explore the chemical composition of the twin domains (100 nm-400 nm). A HIM-SIMS using two gas field ionization sources (He^+ and Ne^+) was utilized for mass-selected chemical imaging of perovskite samples as well as identification of chemical species by spectrum collection in this study. In a positive mode measurement, $CH_3NH_3^+$ (m/z~32) chemical map shows that the $CH_3NH_3^+$concentration differs both in grains and twin domains, however, the Pb^+ (m/z~208) distributes uniformly. These results clarify that the chemical variation between domains originates from $CH_3NH_3^+$ segregation. For the most relevant for the optoelectronic applications of HOIPs, we have shown that this chemical variation affects HOIPs' interaction with light. Combining HIM-SIMS with multiple image techniques, this work offers insight into the fundamental behaviors of the twin domain in $MAPbI_3$, as well as a new line of investigative thought in these fascinating materials.

9:20am **HI+AS-ThM5 Helium and Neon Ion Microscopy for Microbiological Applications*, Ilari Maasilta,*** University of Jyvaskyla, Finland **INVITED**

Imaging of microbial interactions has until now been based on well-established electron microscopy methods. In this talk I review our recent drive to study microbiological samples using a helium ion microscopy (HIM). The main focus will be given on bacterial colonies and interactions between bacteria and their viruses, bacteriophages, which we imaged in situ on agar plates [1]. Other recent biological applications will also be briefly discussed. In biological imaging, HIM has advantages over traditional scanning electron microscopy with its sub-nanometer resolution, increased surface sensitivity, and the possibility to image nonconductive samples. Furthermore, by controlling the He beam dose or by using heavier Ne ions, the HIM instrument provides the possibility to mill out material in the samples, allowing for subsurface imaging and in situ sectioning.

Here, we present the first HIM-images of bacterial colonies and phage–bacterium interactions are presented at different stages of the infection as they occur on an agar culture. The feasibility of neon and helium milling is also demonstrated to reveal the subsurface structures of bacterial colonies on agar substrate, and in some cases also structure inside individual bacteria after cross-sectioning. The study concludes that HIM offers great opportunities to advance the studies of microbial imaging, in particular in the area of interaction of viruses with cells, or interaction of cells with biological surfaces.

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11:00am **HI+AS-ThM10 Characterization of Soot Particles by Helium Ion Microscopy**, ***André Beyer***, *D. Emmrich, M. Salamanca, L. Ruwe, H. Vieker, K. Kohse-Höinghaus, A. Gölzhäuser,* Bielefeld University, Germany

Complementary techniques for the characterization of soot particles are needed to gain insight into their formation processes. In this contribution, we focus on Helium Ion Microscopy (HIM) which allows high contrast imaging of soot particles with sizes down to 2 nm. Soot formation was realized with well-defined model flames from different fuel compositions. The particles were sampled on silicon substrates at different positons within the flame which allows choosing the particles degree of maturity. Large numbers of particles were recorded with a single HIM image in a relatively short time. A number of such images were combined to obtain meaningful particle size distributions. In addition, the following geometric properties of soot particles were evaluated: sphericity, circularity, and fractal dimension. Comparison with other experimental techniques as well as theoretical model calculations demonstrate the strength of the HIM characterization method [1-3].

[1] M. Schenk et al., ChemPhysChem 14, 3248 (2013).

[2] M. Schenk et al., Proc. Combust. Inst. 35, 1879 (2015).

[3] C. Betrancourt et al., Aerosol Science and Technology 51, 916 (2017).

11:20am **HI+AS-ThM11 Development of a Surface Science Spectra Submission Form for Low Energy Ion Scattering (LEIS)**, *M.R. Linford,* ***Tahereh Gholian Avval,*** Brigham Young University*; H.H. Brongersma, T. Grehl,* IONTOF GmbH, Germany

Historically, Surface Science Spectra (SSS) has been an important archive for X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and time-of-flight secondary ion mass spectrometry (ToF-SIMS) data; this detailed, peer-reviewed database now consists of thousands of submissions and spectra that represent these techniques. Thus, SSS has been and continues to be a valuable resource to the surface community. Recently, SSS has begun to expand the surface/material techniques it covers. For example, it now accepts spectroscopic ellipsometry submissions on the optical properties of materials. It is anticipated that submissions in this area will slowly increase so that SSS will become a valuable source of information in this area as well.

In this presentation we discuss the development of an SSS submission form for low energy ion scattering (LEIS). Fields in the form that will be discussed include the abstract, introduction, data, and conclusions. In an SSS submission, the provenance of the sample is carefully documented. A detailed description is also required of the equipment used and of all of its relevant operating parameters – the nature of its beams, the beam energies, the analyzer geometry, etc. The original data collected by the submitter must be supplied, and representative examples of it must be plotted.

Finally, we will show sample submissions based on this new form that should have been submitted for publication by AVS 2018. These will include LEIS submissions of CaF_2, SrO, and Al_2O_3 reference materials

11:40am **HI+AS-ThM12 Time of Flight Backscatter and Secondary Ion Mass Spectrometry in the Helium Ion Microscope**, ***Nico Klingner***, *R. Heller, G. Hlawacek, J. von Borany, S. Facsko,* Helmholtz Zentrum Dresden-Rossendorf, Germany

Existing Gas Field Ion Source (GFIS) based focused ion beam (FIB) tools suffer from the lack of a well integrated analytic method that can enrich the highly detailed morphological images with materials contrast. While Helium Ion Microscopy (HIM) technology is relatively young several efforts have been made to add such an analytic capability to the technique. So far, ionoluminescence, backscattering spectrometry (BS), and secondary ion mass spectrometry (SIMS) using a magnetic sector or time of flight (TOF) setups have been demonstrated.

After a brief introduction to HIM itself and a summary of the existing approaches I will focus on our own time of flight based analytic approaches. TOF-HIM is enabled by using a fast blanking electronics to chop the primary beam into pulses with a minimal length of only 20 ns. In combination with a multichannel-plate based stop detector this enables TOF backscatter spectrometry (TOF-BS) using He ions at an energy of only 30 keV. The achieved lateral resolution is 54 nm and represents a world record for spatially resolved backscattering spectrometry.

Finally a dedicated extraction optics for positive and negative secondary ions has been designed and tested. The setup can be operated in point and shoot mode to obtain high resolution SIMS data or in imaging mode to obtain lateral resolved maps of the sample surface composition. First experiments revealed a very high relative transmission of up to 76% which is crucial to collect enough signal from nanoparticles prior to their complete removal by ion sputtering. The mass resolution of 200 is sufficient for many life science applications that rely on the isotope identification of light elements (e.g.: C, N). The lateral resolution of 8 nm has been evaluated using the knife edge method and a 75%/25% criterion which represents a world record for spatially resolved secondary ion images.

12:00pm **HI+AS-ThM13 Helium and Neon Focused Ion Beam Hard Mask Lithography on Atomic Layer Deposition Films**, ***Matthew Hunt,*** California Institute of Technology*; J. Yang,* University of Texas at Austin*; S.A. Wood, O.J. Painter,* California Institute of Technology

A hard mask lithography technique has been developed wherein a helium or neon focused ion beam (FIB) is used to directly etch a pattern into a thin, atomic layer deposition (ALD) film before then transferring the pattern into the underlying material using a reactive ion etch (RIE). The technique takes advantage of small He-FIB and Ne-FIB probe sizes, capable of directly etching patterns with feature sizes on the order of 1s and 10s of nanometers, respectively, while sidestepping several negative consequences associated with direct etch, namely that low sputter rates prevent large-area patterning from being carried out efficiently, with straight sidewalls, and/or without inducing substrate swelling. An example of the technique is presented here in which (1) 4-10 nm of ALD aluminum-oxide is applied as the hard mask on a 60 nm thick film of aluminum, (2) a <10 pC/um Ne-FIB dose is used to pattern lines that barely etch through the hard mask, and (3) a $Cl_2/CH_4/H_2$ RIE is used to etch the underlying aluminum in 10s of seconds. Neon FIB writing time is reduced by a factor of 20 or more compared to directly etching through the full 60 nm aluminum film. Nanowires as thin as 25 nm are produced with straight sidewalls on 70 nm pitch. This example is being utilized to make superconducting quantum circuit components, e.g. 4 mm long nanocoil inductors that fit into a (20x20) um^2 area. The technique has potentially wide-ranging nanofabrication applications given its amenability to different ALD/substrate material sets and compatibility with both He- and Ne-FIB.

Thin Films Division

Room 102A - Session TF+AS+EL+PS-ThM

In-situ Characterization and Modeling of Thin Film Processes

Moderator: Thomas Riedl, University of Wuppertal

8:00am **TF+AS+EL+PS-ThM1 Defects in Thin Films: A First Principles Perspective**, ***Douglas Irving***, *J.S. Harris, J.N. Baker, S. Washiyama, M.H. Breckenridge,* North Carolina State University*; P. Reddy,* Adroit Materials*; R. Collazo, Z. Sitar,* North Carolina State University **INVITED**

Realization of next-generation power and optoelectronic devices depends on the ability to controllably donor dope thin films of AlN and Al-rich AlGaN. The challenge in donor doping these materials begins with the donor dopant itself, Silicon. While it is a common shallow donor dopant in GaN, it exhibits a deeper ionization level in AlN due to the formation of a DX center near the conduction band minimum. Compensation in both the low and the high doping regime also presents a significant technical challenge to the doping of AlN thin films. In this talk, we explore the mechanisms for compensation in Si-doped AlN in the low and high doping regimes. For this purpose, we have implemented first principles density functional theory calculations with screened hybrid exchange-correlation functionals to determine the properties of individual defects in AlN. The formation energies of each defect are used within a grand canonical equilibrium model to identify the predominant defects as a function of growth conditions. In the low doing regime, important to drift layers in power electronics, we find unintentional impurities and unintentional impurity complexes are often responsible for free carrier compensation. Compensation in films that are doped to higher impurity concentration is found to be related to vacancy-dopant complexes. Possible solutions unique to thin films have also been explored and will be presented. Results from these methods are compared with complementary experimental data that includes below band gap optical absorption and photoluminescence, electrical measurements, dopant implantation, and available SIMS measurements.

8:40am **TF+AS+EL+PS-ThM3 Advances in Numerical Simulation of SiN ALD*, Paul Moroz,*** TEL Technology Center, America, LLC

Atomic layer deposition (ALD) includes a fast growing area of applications and could be foreseen as becoming one of the leading semiconductor technologies. In many cases, it allows accurate atomic-scale deposition of films with almost conformal profiles. Here we present new results on the Monte Carlo feature-scale simulations of ALD conducted with a feature-profile simulator, FPS3D [1-5], as well as comparison of obtained simulation results with the corresponding experiments. The ALD processes are often complex, involving large molecules and, to our knowledge, have not been addressed by other feature-profile simulations except FPS3D. The main factor of all of ALD schemes is the cyclic change in flux parameters and in the corresponding surface chemistry, which results in a single monolayer or, most typically, in a fraction of a monolayer of a film deposited after application of a cycle. Here, we consider a case of ALD with two time-steps: (1) dichlorosilane gas and (2) ammonia plasma. The SiN deposition rate in this case is about a half of a monolayer per cycle. A set of surface reactions is considered which emphasize the steric hindrance effect that was found to be an important factor in explaining deposition rates for this ALD process.

References:

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9:00am **TF+AS+EL+PS-ThM4 Diffusion Kinetics Study of Adatom Islands: Activation Energy Barriers Predicted using Data-driven Approaches*, ShreeRam Acharya,*** *T.S. Rahman,* University of Central Florida

The Self-Learning Kinetic Monte Carlo (SLKMC) method [1] with a pattern recognition [2] and a diffusion path finder scheme enables collection of a large database of diffusion processes including single- and multiple-atoms, and concerted island motion and their energetics. The databases collected from adatom-island (2-8 atoms) diffusion characteristics for a large set of homo- and hetero-epitaxial metallic systems (Cu, Ni, Pd and Ag) are used to extract a set of easily accessible features, geometrical and energetic, using physical insight which are then encoded. Those features along with activation energy barrier are used to train and test linear and non-linear statistical models. A non-linear model developed based on neural network technique predicts the diffusion energy barriers with high correlation with the calculated ones. In this talk, we present the results of kinetics study of these homo or hetero-epitaxial metallic systems some of whose barriers are used for training of the model and are compared to the corresponding quantities obtained from KMC simulation using energy barriers calculated from computationally intensive interatomic interaction potential based approach.

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Work supported in part by MMN-1710306.

9:20am **TF+AS+EL+PS-ThM5 Using Ellipsometry and XPS to Understand the Degradation of Thin-film Aluminum Mirrors Protected by Ultrathin Fluorides***, M.R. Linford,* ***Brian I. Johnson****, R.S. Turley, D.D. Allred,* Brigham Young University

The LUVOIR (Large, UV-optical-IR) telescope is a potential NASA flagship space-based observatory of the 2020's or 30's. It will utilize the largest mirrors ever put into space. The reflective coating for the mirrors will be aluminum, since there is no material with comparable reflectance at shorter wavelengths. However, to achieve high reflectance over the broadest energy range, the top surfaces of such Al mirrors must be protected against the formation of oxide layers that form quickly in air using wide-bandgap fluoride coatings, traditionally about 25 nm of MgF_2. Researchers have been endeavoring to use fluorides which are transparent further into the VUV (vacuum ultraviolet) like LiF and AlF_3, and to make these barriers more continuous by depositing them on heated surfaces and making the barriers thinner. However, when the barriers are thinner and when materials like LiF are exposed to moist air, degradation of VUV reflectance is observed. Thus, studying fluoride barrier-coated mirrors is vital. We have recently reported on the time dependent growth of apparent aluminum oxide thickness for two Al mirrors protected by ultrathin fluoride layers. These measurements were based on variable-angle, spectroscopic ellipsometric (VASE) measurements. (Allred, Thomas, Willett, Greenburg, & Perry, 2017) (Miles, 2017) . VASE, however, does not provide chemical composition data. An independent analytical technique which is sensitive to surface composition is required. We have undertaken such investigations using X-ray photoelectron spectroscopy (XPS), and now report on correlations between optical properties and XPS for fluoride-coated aluminum mirror test structures.

9:40am **TF+AS+EL+PS-ThM6 Model for Amorphous Thin Film Formation and Validation*, Rahul Basu,*** VTU, India

A coupled set of equations describing heat and mass transfer during phase transformation is formulated The model is extended to incorporate surface convective effects. These equations which are non linear due to the moving interface are linearized and decoupled. Effects of various heat transfer parameters are analyzed through small parameter expansions. Solutions obtained via this artifice allow closer examination of surface effects on the boundary layer of the phase transformation. A relation is found for the effect of the glass transition temperature versus the boundary layer thickness for several alloys in various groups of the Periodic Table. Earlier work and results are analyzed in light of the present analysis.

11:00am **TF+AS+EL+PS-ThM10 2D TMD Monolayer of MoS_2 BY ALD and Insight in the Mechanism by Surface Organometallic Chemistry*, Elsje Alessandra Quadrelli,*** CNRS CPE Lyon, France **INVITED**

Atomically-thin crystalline domains of MoS_2 [1] or WS_2 [2] are obtained from an organometallic amorphous deposit obtained by ALD/MLD.

This original result with respect to the state of the art has been mechanistically rationalized with in situ and in operando modelling studies on the oxide nanobeads at different annealing temperatures. This contribution will present the surface organometallic method, the characterization of the 2D layers (among which the first in-plane micrographs of ALD-grown MoS_2 samples)[1] and the proposed surface coordination chemistry mechanism at hand obtained with model studied on 3D silica beads. These model studies couple in operando infra-red spectroscopy, gas-chromatography detection of the released by-products and atomic composition of the deposit at each cycle, leading to molecular level understanding of the growth process.

***Acknowledgments** : This work was carried out within the framework of the partnership between the C2P2 research unit (UMR 5265 CNRS CPE Lyon University Claude Bernard Lyon 1) and CEA's Directorate of Technological Research (DRT) on the nanochemistry platform installed in CPE Lyon. The authors of the papers below thank CPE Lyon, CNRS, CEA / LETI (Silicon Technology Department and nanocharacterization platform) for the support and the DRF / INAC for the collaboration in the framework of the "2D Factory" project.*

***Ref** : [1] Cadot et al.Nanoscale , **2017**, 9, 467. [2] Cadot et al. JSVT A **2017**, 35, 061502 .*

11:40am **TF+AS+EL+PS-ThM12 A Novel Fourier Transform Ion Trap Mass Spectrometer for Semiconductor Processes*, Gennady Fedosenko,*** *H.-Y. Chung, R. Reuter, A. Laue, V. Derpmann, L. Gorkhover, M. Aliman, M. Antoni,* Carl Zeiss SMT GmbH, Germany

Real-time inline control of process gas compositions with high sensitivity has been of particular importance in recent years in the semiconductor industry and beyond. Commonly quadrupole residual gas analyzers (RGA) are used, together with Optical Emission Spectroscopy (OES) for process control and process development. However, most RGAs are not capable of measuring a whole mass spectrum fast enough to monitor etch or deposition processes of a few seconds. A new process control mass spectrometer, based on Fourier-Transform 3D Quadrupole Ion Trap technology, is more appropriate for real-time inline process monitoring.

The 3D-Quadrupole Ion Trap mass spectrometer *iTrap*® by ZEISS is installed in a vacuum chamber (~ 120mm x 120mm x 500mm) with a fast switching valve for pulsed gas sample injection (pulse duration ~ 50ms or less). An electron gun is used for ionization of the gas pules. The Ion Trap achieves ion trapping and accumulation by means of a radio frequency applied to the ring electrode of the trap. With the aid of advanced electronic amplifiers and selective ion excitation technique the ion oscillations can be measured electrically by means of the induced current on the cap electrodes without using any separate particle detector. The mass spectrum can be finally obtained in less than one second.

Real-time measurements of the hydrogen plasma cleaning process of Sn contaminated samples were performed with the *iTrap* mass spectrometer. The working pressure of the plasma cleaning process was 0.5 mbar. Decreasing signal of SnH_4 and other contaminations from the samples which are directly correlated to the cleaning process were observed with *iTrap*. This result is extremely useful for the process control of plasma processes and inline real-time contaminations control for high-end applications.

Inline measurement at a MOCVD chamber showed that *iTrap* is capable to detect reaction products, contaminations on the wafer holder and dopant memory in real-time. These results demonstrate that *iTrap* is a very sensitive and fast process mass spectrometer suitable for real-time inline process monitoring.

Many etch processes take place in 10 to 30 s process steps. Different processes were examined with e.g. HBr or BCl_3 chemistry together with several wafer materials such as Silicon, Hafnium Oxide or Titanium Nitride. The obtained mass spectra show the etch plasma chemistry together with etch reaction products (HfClx, SiClx, etc.). This data gives new insight into the etch processes, which until now were rarely understood on a chemical level. First wafer effects related to the chamber cleaning and pre-coating steps prior to the etch step were also examined.

12:00pm **TF+AS+EL+PS-ThM13 Realization of Shifts in Threshold Voltage and Subthreshold Swing in Atomic Layer Deposited Zinc Oxide As Channel Layer through *in-situ* Half-Cycle Analysis***, **Harrison Sejoon Kim**, A.T. Lucero, S.J. Kim, J. Kim,* University of Texas at Dallas

Thin film process monitoring of atomic layer deposition (ALD) has been adopted as the versatile technique to identify both chemical and physical properties of ALD films. Their *in-situ* characterization technique includes mostly Fourier-transform infrared spectroscopy, X-ray photoelectron spectroscopy, and quartz crystal microbalance analysis. [1–3] However, currently there are no reports on monitoring the results of sub-nm device physics even if we are already in the era of beyond 10 nm node semiconductor processes. Moreover, even if there are a few initial studies, demonstrating *in-situ* electrical characterization with ALD, it requires device packaging, which ultimately limits the flexibility to be further characterized. [4]

In this current work, we have developed an ultra-high vacuum (UHV) cluster tool equipped with thermal processing, plasma surface treatment, thin film deposition, and electrical characterization which can be performed *in-situ* (Figure 1). With this feasibility, we demonstrate the deposition of semiconducting zinc oxide (ZnO) in inverted-coplanar structured thin film transistors (TFT). Diethylzinc (DEZ) and water (H_2O) is used as ALD precursors at 100°C. DEZ and H_2O half-cycle analysis is carried out to monitor the interface states of ZnO/dielectric (Figure 2). Initially, 45 ALD cycles of ZnO have shown switching behavior with an on/off ratio of ~10^2 in vacuum. Subsequent ALD cycle shifts the threshold voltage (V_{th}). V_{th} shifts associated with each ALD cycle are assumed to be attributed to the changes in interface trap density as a result of interface state passivation in ZnO during its growth, especially passivating fixed oxide charges (Q_{ox}). To understand interface states of ZnO and the bulk of oxide better, further analysis of shift of subthreshold swing (SS) is demonstrated. Since shifts in SS best represents changes in interface trap density, [5] it is worthwhile to note the changes in SS in metal-oxide-semiconductor transistors.

This work was supported by the Creative Materials Discovery Program on Creative Multilevel Research Center (2015M3D1A1068061) through the National Research Foundation(NRF) of Korea funded by the Ministry of Science, ICT & Future Planning.

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Applied Surface Science Division
Room 204 - Session AS+NS-ThA

Profiling, Imaging and Other Multidimensional Pursuits

Moderators: Ashley Ellsworth, Physical Electronics, Jordan Lerach, ImaBiotech Corp.

2:20pm **AS+NS-ThA1 Surface Science Study of Au/Ni/Cr/n-SiC and Au/Cr/Ni/n-SiC Thin Film Ohmic Contact Material***, **Martyn Kibel**,* La Trobe University, Australia*; A.J. Barlow,* La Trobe University, Australia*; P.W. Leech,* RMIT University, Australia

Silicon carbide (SiC) has become a promising semiconductor material for use in elevated temperature and high power devices. Although ohmic contacts to n-SiC have been widely fabricated using a metallization of Ni/n-SiC annealed at ~1000 °C, the formation of nickel silicides at the interface has resulted in uneven roughening of the metal surface. We have examined for the first time the development of ohmic contact materials containing layers of both Ni and Cr (Au/Ni/Cr/n-SiC and Au/Cr/Ni/n-SiC). A detailed study of these layered structures, both as-deposited and subsequently annealed at 750-1000°C has been undertaken using a range of surface analysis techniques. Auger electron spectroscopy (AES) depth profiling, both static and using Zalar rotation, has been used to etch through the layers into the epitaxial SiC. AES elemental mapping, in conjunction with SEM imaging, has been used to record the nature of the surface before and after profiling. AES line scans have also been employed to characterize the subsequent crater walls. In addition, X - ray photoelectron spectroscopy (XPS) depth profiling has been used to characterise the interfaces with a focus on the chemical states of the constituent elements. The nature of the interfaces between individual layers is discussed as well as the methodologies for generating depth profiles from the acquired data. The analysis has shown a wide-scale interdiffusion of the layers after annealing of the Au/Ni/Cr/n-SiC structure with the formation of surface globules. In comparison, the Au/Cr/Ni/n-SiC contacts have shown a limited interdiffusion of the layers and relatively smooth surfaces, indicating that the intermediate layer of Cr has acted as a diffusion barrier for the Ni. The electrical characteristics of the as-deposited and annealed contacts have been measured using circular transmission line test patterns and the results correlated with the AES and XPS analyses.

2:40pm **AS+NS-ThA2 3D Imaging of InGaN/GaN based Nanowires and Nanotubes using Time-of-flight Secondary Ion Mass Spectrometry***, **Jean-Paul Barnes**,* Univ. Grenoble Alpes, CEA, LETI, France*; A. Kapoor,* Univ. Grenoble Alpes, CEA, France*; C. Durand,* Univ. Grenoble Alpes, CEA, France*; C. Bougerol,* Univ. Grenoble Alpes, CNRS, France*; J. Eymery,* Univ. Grenoble Alpes, CEA, France

GaN based nanowire light-emitting diodes (LEDs) can be grown in ordered arrays on sapphire and large Si substrates. The growth of coaxial InGaN/GaN multiple quantum wells (MQWs) on the nonpolar m-plane sidewalls of the GaN wire increases the active region area, reduces the defect density and can increase efficiency in the case of thick QWs due to the absence of quantum confined Stark effect [1]. Variants on this approach include InAlN/GaN MQW tubes and the integration of such wires in flexible substrates [2].

An important parameter controlling the light emission is the indium concentration in the MQWs and their thickness, which may vary along the length of the wire. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) has been used to perform 3D mapping of the indium concentration in the coaxial MQWs for both GaN wire geometries and InAlN/GaN MQW tube geometries.

Experiments are performed using a dual beam approach with a finely focused (<200 nm spot size) Bi_3^{++} analysis beam at 60 keV and oxygen sputtering at 500 eV. The indium concentration is calibrated from a 2-D MQW structure on which the nanowires are deposited for analysis so that TOF-SIMS analysis can be performed on the sidewall perpendicular to the MQWs. The TOF-SIMS analysis on single nanowires has allowed the composition of InGaN quantum wells to be quantified and the fact that the MQW structure becomes thicker towards the end of the nanowire to be determined. The ability to target specific nanowires allows the composition determined by TOF-SIMS to be compared with photoluminescence and cathodoluminescence measurements to link the emission of the wires to the MQW composition and thickness. Using a similar approach it was possible to characterize the InAlN/GaN MQWs on nanotube structures and confirm that the MQW structure remains after selective etching of the GaN core and annealing. Such high resolution TOF-SIMS 3D imaging can also be used for other semiconductor structures such as those grown by selective epitaxial growth of for visualising doping in microelectromechanical systems (MEMS) systems.

This work was carried out on the nanocharacterisation platform (PFNC) of the CEA Grenoble.

References:

R. Koester et al. "M-plane core-shell InGaN/GaN multiple-quantum-wells on GaN wires for electroluminescent devices," Nano Letters **11** (11), 4839-4845 (2011).

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3:00pm **AS+NS-ThA3 Atom Probe Tomography: Applications and Prospects for Surface and Interface Science***, **Austin Akey**, D.C.. Bell,* Harvard University **INVITED**

Atom Probe Tomography (APT) is a three-dimensional, individual-atom composition mapping technique. Specimens are disintegrated atom-by-atom using a combination of high electric fields and voltage or laser pulses, causing individual ions to be ejected towards a position-sensitive detector with high time resolution. The resulting hit position, combined with the ion's time of flight, allows single-Angstrom, single-atom time-of-flight mass spectroscopy to be performed over volumes containing hundreds of millions to billions of atoms. Recent advances in instrument design and automation have greatly expanded the field of materials systems and scientific questions that the technique can address, and it is particularly well suited to analysis of surface and interface composition.

Datasets can be processed and analyzed as highly-localized 1D composition measurements, 2D surface mapping over an arbitrary surface in three-dimensions, or full volumetric composition maps, allowing a wide variety of questions to be asked of a material. We present applications including: bulk composition fluctuation and clustering measurements; full 3D composition mapping of electronic devices; interface composition and roughness determination; composition mapping of nanowire and other quasi-one-dimensional structures; and surface and bulk composition of catalytic materials. We also discuss the importance of correlating other microanalysis techniques with APT and give examples of one-to-one correlative work. The development of correlative electron microscopy and APT specimen geometries have allowed otherwise unresolvable questions to be answered, and new work extends this into the realm of combined in-situ and ex-situ measurement of the structural and compositional evolution of materials. Finally, we will discuss future prospects for the technique and its application to surface science.

4:20pm **AS+NS-ThA7 Industrial Applications of Surface Analysis in Chemical Mechanical Planarization***, **Hong Piao**, Y.N. Liang, J. McDonough, C. Ballesteros,* FUJIFILM Planar Solutions, LLC, FUJIFILM Electronic materials USA., Inc.*; E. Turner,* FUJIFILM Planar Solutions, LLC, FUJIFILM Electronic materials USA., Inc*; A. Mishra, R. Wen,* FUJIFILM Planar Solutions, LLC, FUJIFILM Electronic materials USA., Inc.

Chemical mechanical planarization/polishing (CMP) is a chemical reaction assisted mechanical polishing process in the semiconductor manufacturing industry to remove overburden material or specific layers in the film stacking and to planarize the topography at the patterned wafer surface. Although the basic principles of CMP are understood, thorough understanding of surface chemical processes which occur during polishing is still lacking, especially the chemistry at the interface of the wafer/slurry/pad. Investigations aimed at understanding fundamental mechanisms usually employ electrochemical techniques. Surface analysis methods remain rather under-utilized in this field, especially when taking into account the explosive growth of these surface techniques for the analysis of "nano-structured" films in other research fields.

FUJIFILM Planar Solutions (PLNR) is a market leader for metals and dielectric CMP slurries. Our in-house XPS and ToF-SIMS surface analysis tools have greatly enhanced our capabilities in analyzing and understanding surface reactions, their mechanism, and fundamental science and engineering behind the slurry wafer interaction at the interface during CMP.

The goal of this presentation is to review selected results provided by advanced surface analysis tools combined with other complementary testing methods. Examples describing CMP characterization are given in two technological areas that are growing in importance: (1) Cu and Co CMP and (2) Defectivity in front end of line polishing involving dielectrics. We also pay particular attention to show how the recent improvements in instrumentation could open new opportunities and fundamental understanding of how surface analyses can enable improvements in slurry design for CMP, thus leading to the development of next-generation advanced CMP slurries and processes.

4:40pm **AS+NS-ThA8 Correlative Images of Microscopy Spectroscopy: Beyond the 3D Characterization in Surface Analysis***, **Tanguy Terlier,*** Korea Institute of Science and Technology, Republic of Korea*; R. Verduzco,* Shared Equipment Authority, Rice University*; Y. Lee,* Korea Institute of Science and Technology, Republic of Korea

Technological progress has spurred the development of increasingly sophisticated analytical devices. The full characterization of structures in terms of sample volume and composition is now highly complex. Traditionally, the surface spectroscopic techniques such as AES or ToF-SIMS provide the chemical distribution of sample surfaces. Nevertheless, an important issue in surface analysis is to perform 3D chemical mapping of structured samples with a complex architecture, conserving as well high spatial resolution (lateral and in-depth) as high mass resolution. During the surface analysis, only a projection into 2D surface mapping is achieved which reverse the topographic render after the in-depth analysis. Moreover, the use of ion beam sputtering induces preferential sputtering and damage accumulation due to the sputter beam. So, the surface roughness generated by the sputtering affects the depth profiling of chemical signals. In consequence, the authentic 3D chemical distribution as a function of the depth is completely distorted or lost.

Alternative approaches to resolve the artifacts of 3D chemical images exist. Among these solutions, the use of Scanning Probe Microscopy (SPM) in combination with a surface spectroscopic analysis permits to correct the depth scale of the data and to reduce the artifacts due to the depth profiling. In addition to the data correction, correlative approach using SPM and surface spectroscopy offers the unique possibility to couple topography with 3D chemical information for having access to the accurate volume render. Merging other measurable signals such as electrostatic force microscopy with 3D chemical analysis can also enhanced the understanding of the surface properties and structure characteristics.

After a brief introduction to the data fusion, different methods of 3D reconstruction used in surface analysis will be discussed. In particular, we will show a recent method, the dynamic-model-based volume correction. This method has been applied on a patterned sample using two combination of techniques, SPM/ToF-SIMS and SPM/AES. Then, we have compared the performances of *ex situ* SPM/ToF-SIMS with a new instrument, an *in situ* SPM/ToF-SIMS. To illustrate the new potentials of the correlative imaging method, we have characterized two different samples, a cryo-freezing prepared cell sample and a self-assembled block copolymer film. Finally, we will explore the applications of the correlative microscopy and spectroscopy analyzing a standard SRAM sample that is composed of patterned structures integrating concentration-controlled doping. This sample has provided multi-signal mappings and a quantitative analysis.

5:00pm **AS+NS-ThA9 3D Structure of Atomically Dispersed Metal Species on an Oxide Single Crystal Surface Studied by Polarization-dependent Total Reflection Fluorescence (PTRF)-XAFS***, **Satoru Takakusagi**, K. Asakukra,* Hokkaido University, Japan

Precise size control of metal species on an oxide surface, especially in the range of <1 nm, is now highly important to develop the next-generation catalysts, sensors, and electronic devices. However this is not easy since metal atoms are easily aggregated to form large particles on an oxide surface. This is due to the small stabilization energy and/or the small activation energy for the metal diffusion. If one can obtain a monatomic metal species on an oxide surface, it can be a building block for synthesis of the metal cluster and helps us to control the cluster size in one-atom precision. Our group has developed the "premodified surface method" to obtain a highly dispersed metal species on an oxide single crystal surface. In the premodified surface method, the oxide surface is precovered with a functional organic molecule possessing a substituent atom which can strongly coordinate to a metal atom before metal deposition. We have determined the precise 3D structures of such metal species by polarization-dependent total reflection fluorescence (PTRF)-XAFS technique.

In this study, various metals such as Cu, Au, Ni and Pt were vacuum-deposited on a $TiO_2(110)$ surface premodified with *o*-mercaptobenzoic acid (*o*-MBA) and their 3D structures were determined by the PTRF-XAFS technique. We have found that Cu, Au and Ni were atomically dispersed by bond formation with sulfur of *o*-MBA and oxygen in the TiO_2 lattice, but Pt was aggregated to form clusters. We will discuss the factors that govern single metal dispersion based on the energy difference between sulfur−metal−oxygen and metal−metal bond formations.

5:20pm **AS+NS-ThA10 XPS Imaging and Spectromiscroscopy Investigation of Extended Release Pharmaceutical Tablets***, **Jonathan Counsell**, S.J. Coultas, C.J. Blomfield,* Kratos Analytical Ltd, UK*; D.J. Scurr,* The University of Nottingham, UK*; L. Mason,* University of Nottingham, UK*; V. Ciarnelli, J.M. Garfitt, S. Rigby-Singleton,* Juniper Pharma Services Ltd, UK*; M.R. Alexander,* The University of Nottingham, UK*; M.C. Davies,* University of Nottingham, UK*; C. Moffitt,* Kratos Analytical Inc.*; S.J. Hutton,* Kratos Analytical Ltd, UK

The effects of formulation methodology on the performance of tablets have been studied for decades. Typically tablets consist of the active drug and excipients which influence stability, release rate and binding. HPMC (Hydroxypropyl Methylcellulose) is a hydrophilic polymer commonly used in extended-release tablets as it shows rapid hydration and uniform gel formation. The microstructure of HPMC particles in matrices influences the ability of HPMC to form gel layers after contact with water, thereby affecting release characteristics. While previous studies described the use of Raman spectroscopy as a benchmark method for chemically imaging solid pharmaceutical formulations[1], there are relatively few contributions reporting the application of XPS (X-ray Photoelectron Spectroscopy) in this field. New insight into tablet component distribution could be employed in the successful formulation design and development process.

Herein we investigate the novel application of XPS to elucidate the distribution of both drug and excipients species. Parallel XP imaging capabilities will be illustrated and demonstrated for several tablet systems yielding information on particle size, distribution and shape. The use of small-spot XPS provides quantitative and chemical-state information on imaging features. The novel use of argon cluster ion bombardment will be discussed for both cleaning and depth profiling. Peak-fitting, pitfalls and limitations will be explored and compared with other complementary techniques such as ToF-SIMS.

Strachan *et al*. Journal of Pharmacy and Pharmacology. 2007. 179-192.

5:40pm **AS+NS-ThA11 An experimental Guide to Conversion of Tof-SIMS Spectrum to BIG DATA: Application in Analysis of Ultrathin Coatings***, **Kevin Abbasi**, A.A. Avishai,* Swagelok Center for Surface Analysis of Materials, Case school of Engineering, Case Western Reserve University

Thin films are traditionally being characterized using cross sectional analysis with scanning or transmission electron microscopes. Although accuracy of these technique are very high, it's hard to analyze a large number of samples this way. Surface analysis instruments such as X-ray photoelectron spectroscopy (XPS), Auger Electron Spectroscopy (AES) and Time-of-flight secondary ion mass spectrometry (Tof-SIMS) can be used to analyze the top surface and erode it with focused ions. Alternating the analysis and ion etching cycles, concentration profiles can be achieved.

In specific conditions where the element of interest has very low concentration or the thickness of the coating is less than the analysis volume (ultrathin films), Tof-SIMS becomes a very powerful tool as it provides the best detection limit and smallest analysis depth. Extracting useful and specific information from the mass spectra and reducing the dimensionality of very large datasets, is a challenge, that has not been fully resolved. Multivariate analysis has been widely deployed to assist in the interpretation of the Tof-SIMS data. Principal component analysis is a popular approach that can help ease the task of analyzing spectrums acquired at different locations from the top surface, compare it against different samples and help extract trends.

The purpose of this talk is to provide experimental guide for the characterization of ultrathin coatings (both flat and in form of particles). Two set of samples will be described: Inter-diffusion will be characterized in a flat coating obtained from Atomic layer deposition (ALD) process and contamination analysis will be then discussed on micron size particles with ultrathin coating. Different strategies will be then discussed to obtain concentration profiles using Time-of-flight secondary ion mass spectrometry. Principal component analysis will then be used to successfully convert mass spectrums into big data and extracting similarities between spectrums and samples.

Nanometer-scale Science and Technology Division
Room 102B - Session NS+2D+AS+MN+PC-ThA

SPM – Probing Electronic and Transport Properties

Moderators: Ondrej Dyckoe, Oak Ridge National Laboratory, Sergei Kalinin, Oak Ridge National Laboratory, Indira Seshadri, IBM Research Division, Albany, NY

2:20pm **NS+2D+AS+MN+PC-ThA1 Imaging Currents in Two-dimensional Quantum Materials***, **Katja Nowack**,* Cornell University **INVITED**

Magnetic imaging is uniquely suited to the non-invasive imaging of current densities, particularly in two-dimensional devices. In this talk, I will showcase this approach by discussing measurements on HgTe quantum well devices in the quantum spin Hall (QSH) regime. In a nutshell, we scan a superconducting quantum interference device (SQUID) to obtain maps of the magnetic field produced by the current flowing in a device. From the magnetic image we reconstruct a two-dimensional current distribution with a spatial resolution on the micron scale. This allows us to directly visualize that most of the current is carried by the edges of the quantum well devices when tuned into their insulating gaps - a key feature of the QSH state. I will both discuss routes towards improving the spatial resolution of our measurements to sub-micron length scales through a combination of improved image reconstruction and smaller sensor sizes.

3:00pm **NS+2D+AS+MN+PC-ThA3 Side-gate Construct for Probing Active Energy Levels in Electron Transport through a Solid-state Surface-bound Protein Monolayer***, **Sidney Cohen**, B. Kayser, C. Gua, M. Sheves, I. Pecht, D. Cahen,* Weizmann Institute of Science, Israel

Electron transport studies provide an excellent platform to deduce electronic structure in molecular electronics studies, enabling control and understanding of the pathways and mechanisms involved. Due to their complexity, proteins are used only infrequently in this context, despite convenient properties such as selective binding, self-assembly, light sensitivity, and the possibility to (bio) chemically tailor properties . Here, we study electron transport in monolayer films of Azurin, using a 3-electrode configuration with a novel side-gate. The source and drain are gold substrate and conductive atomic force microscope (C-AFM) probe, respectively. The measuring devices were prepared in a two-step electron beam lithography process, whereby interdigitated drain and gate electrodes with separation of 80 nanometers are patterned from macroscopic electrodes, the latter formed optically on a silicon oxide substrate. The gold electrodes are patterned with the gate elevated by 20 nm for improved coupling with the drain. After deposition of the Azurin monolayer on this structure, the carrier chip was wire-bonded for insertion into the AFM. Azurin was incorporated in the device both as copper-containing holo-Azurin, and as apo-Azurin with the Cu ion removed. Stability of source-drain vs. $V_{source-drain}$ curves, as well as gate-drain leakage were monitored for validity. $I_{source- drain}$ vs. $V_{source-drain}$ curves were acquired at different gate voltages, and $I_{source- drain}$ at 0 $V_{source-drain}$ was measured while sweeping V_{gate} in both polarities. Asymmetry of current onset for opposing gate biases points to a low-lying LUMO transport level for holo-Azurin. For apo-Azurin this level is shifted to higher values and hence inaccessible. Semi-quantitative location of the tail of this LUMO, as well as value of gate coupling were estimated by changing the work function of the drain electrode, i.e. C-AFM probe, from Pt (ϕ=-5.3 eV) to Au (ϕ= -4.9 eV). The observations can be rationalized by considering previous electrochemical and theoretical studies.

3:20pm **NS+2D+AS+MN+PC-ThA4 Adding Electrons One at a Time to Electrostatically Confined Graphene Quantum Dots**, ***Daniel Walkup**, C. Gutierrez, F. Ghahari,* National Institute of Standards and Technology (NIST)/ University of Maryland, College Park*; C. Lewandowski,* MIT*; J. Rodriguez-Nieva,* Harvard University*; T. Taniguchi, K. Watanabe,* National Institute for Materials Science (NIMS), Japan*; L. Levitov,* MIT*; N.B. Zhitenev, J.A. Stroscio,* National Institute of Standards and Technology (NIST)

The Coulomb blockade of adding charges to isolated metallic systems is one of the most characteristic phenomena of quantum dots (QDs). Here, we created circular graphene QDs in a backgated graphene-hexagonal boron nitride (hBN) device by locally ionizing defects in the hBN layer, using the electric field from the tip of a scanning tunneling microscope (STM). Scanning tunneling spectroscopy (STS) enables us to image the local density of states outside and within these circular graphene resonators. At weak magnetic fields, confinement of graphene electrons is poor and Coulomb blockade is not observed. At higher fields, however, the graphene electrons form quantized Landau levels (LLs) separated by energy gaps. In the area of the QD, the LLs are bent by the electrostatic potential creating metallic (compressible) rings where a LL crosses the Fermi energy, separated by circular insulating barriers (incompressible strips), which isolate the dot from the graphene and enable the onset of Coulomb blockade. Tunneling dI/dV spectra inside the QD reveal a series of Coulomb blockade peaks, which shift as a function of back gate voltage. In the plane defined by gate voltage and sample bias, these peaks form Coulomb lines, whose slope is governed by the relative capacitances between the dot, tip, gate, and sample bias electrodes, and whose relative offsets reveal the addition spectrum of the quantum dot. A characteristic feature of the Coulomb blockade in these systems is the presence of different families of charging lines, one for each LL, which intersect each other and experience avoided crossings. The avoidance pattern of these anticrossings is novel: at the strongest fields, it somewhat resembles the predictions of simple models of electrostatically-coupled QDs, but at weaker fields it diverges very strikingly, and new modeling is needed to reproduce it. This avoidance pattern reflects the interaction of electrons in different LLs, occupying different parts of the QD, and is tunable via the magnetic field and gate voltage. By moving the STM tip, we can tune the tip-dot capacitance, and tunnel into different parts of the dot, enabling a full characterization of the anticrossings in these novel electronic nanostructures.

4:00pm **NS+2D+AS+MN+PC-ThA6 Bulk and Surface Contribution to the Charge and Spin Transport in Topological Insulators Observed with a Four-Probe Scanning Tunneling Microscope***, **Wonhee Ko**, G.D. Nguyen,* Oak Ridge National Laboratory*; H. Kim, J.S. Kim,* Pohang University of Science and Technology, Republic of Korea*; A.-P. Li,* Oak Ridge National Laboratory

Topological insulators are fascinating materials for future electronics because of its superior charge and spin transport characteristics stemming from their topological nature. However, topological insulators realized in actual materials have both bulk and surface carriers, where the former significantly hampers the topological transport of the later. In this talk, we utilize four-probe scanning tunneling microscope to investigate bulk and surface contribution to the charge and spin transport in bulk-insulating topological insulator Bi_2Te_2Se. The relative contribution of bulk and surface was varied by changing temperature and transport area, which was measured by variable probe-spacing spectroscopy. The surface dominant regime was already reached at 82 K, where the sample exhibited superior transport properties such as a large surface mobility and high spin polarization. At this regime, the contact to external probes also transforms from Schottky to Ohmic junction. Our result indicates that controlling bulk and surface contribution to the transport is crucial for realizing topological devices.

4:20pm **NS+2D+AS+MN+PC-ThA7 Modulation of Single-Walled Carbon Nanotube Electronic Structure by External Electronic Perturbations: Scanning Tunneling Spectroscopy and Density Functional Theory***, **Benjamen Taber**[1], G.V. Nazin,* University of Oregon

Understanding the local impact of environmental electronic perturbations on the local density of states (LDOS) of single-walled carbon nanotubes (CNTs) is critical for developing CNT-based devices. We present scanning tunneling microscopy and spectroscopy (STM/STS) investigations of CNTs adsorbed on both a metal, Au(111), and a dielectric, monolayer RbI on Au(111), serving as models for stronger and weaker electrostatic interactions, respectively. In both cases, STS revealed modulations in the CNT LDOS corresponding to features in the underlying material. We then corroborate our STM/STS results with density functional theory calculations of the electronic structure of semiconducting CNTs in the presence and absence of an external dipole (a pair of opposite charges). DFT-calculated CNT LDOS quantitatively matched STM/STS results, providing key insight in to the local impact external charges have on CNT electronic structure.

4:40pm **NS+2D+AS+MN+PC-ThA8 Single Charge and Exciton Dynamics probed on the Molecular Scale***, **Anna Roslawska**, P. Merino, C. Grosse, C.C. Leon, O. Gunnarsson, M. Etzkorn, K. Kuhnke, K. Kern,* Max Planck Institute for Solid State Research, Germany

The performance of organic optoelectronic devices depends on the dynamics of charges and excitons (electron-hole pairs). The relevant processes have been mostly studied by time-resolved techniques with a spatial resolution limited by optical diffraction. In order to overcome this limit, a nanoscale scanning probe approach that enables addressing individual light emitters is preferred. Here we introduce time-resolved scanning tunneling microscopy-induced luminescence (TR-STML) and use it

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[1] **NSTD Postdoc Finalist**

to explore locally the single charge and single exciton regime. The excitonic light originates from structural defects in C_{60} thin films on Au(111) that act as charge and exciton traps. Such a defect is a single photon emitter, whose spectrum has a sharp electron-hole recombination feature [1,2]. By measuring the time-resolved electroluminescence due to individual injected charges, it is possible to analyze the formation and recombination processes of single excitons and determine their characteristic time constants[3].

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5:00pm **NS+2D+AS+MN+PC-ThA9 Microscopic Understanding of the Temperature-dependent Carrier Transport in Ge Nano - Crystal s Films***,* ***Dan Shan****,* Yangzhou Polytechnic Institute, China*; J. Xu,* Nanjing Universityy, China

Silica-based semiconductor nano-crystals have attracted much interest in recent years due to their possible applications in many kinds of nano-electronic and optoelectronic devices. Compared with Si, Ge has larger electron and hole mobility. Furthermore, Ge has a narrower band-gap and high phonon responsivity in the near-infrared region, so it is suited to many near-infrared applications. In order to further improve the device performance, detailed knowledge of transport mechanisms across these nano-crystals becomes necessary and is considered indispensable.

In this work, hydrogenated amorphous germanium films were prepared by a plasma enhanced chemical vapor deposition technique. Ge nano-crystals (Ge NCs) films were obtained by thermal annealing the as-deposited samples. P-type behavior in Ge NCs films without any external doping is attributed to the holes accumulation caused by acceptor-like surface states. It can be found that the dark conductivity and Hall mobility reach to as high as 25.4 S/cm and 182 $cm^2/V\cdot s$ in the Ge NCs film, which are much higher than the previously reported data. Carrier transport mechanisms of Ge NCs films were investigated by temperature-dependent Hall measurement. Three kinds of temperature-dependent conductivity behaviors, which exhibit the linear relationships of the ln σ versus $T^{-1/4}$, $T^{-1/2}$ and T^{-1}, respectively, were observed in the temperature regions of 10-500 K. It can be confirmed that the thermal activation conduction in the extended states dominated the carrier transport process above 300 K (300-500 K). Below room temperature, the carrier transport process was dominated by the percolation-hopping conduction at 90-230 K and turned to Mott-VRH conduction when the temperature falling below 50 K (10-50 K).

Furthermore, the different scattering mechanisms in carrier transport process were found in different temperature regions, which were evaluated via temperature-dependent Hall mobilities. In the low temperature region (10-50 K), the carrier Hall mobility is almost temperature independence ($\mu \sim T^0$), revealing the neutral impurities' scattering mechanism dominated the carrier transport process. When increasing the temperature (50-190 K), the carrier transport properties were controlled by the grain boundary scattering mechanism, where the carrier Hall mobility was increased with temperature and exhibited the thermally activated behavior. However, the relationship of $\mu \sim T^{-0.9}$ was observed above room temperature (300-500 K). It is suggested that the carrier transport is dominated by a superposition of grain boundary scattering and acoustic phonon scattering within the high temperature region.

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic
Room 202A - Session SA+AS+HC+SS-ThA
IoT Session: Multi-modal Characterization of Energy Materials & Device Processing

Moderators: Maya Kiskinova, Elettra-Sincrotrone Trieste, Italy, Slavomir Nemsak, Advanced Light Source, Lawrence Berkeley National Laboratory

2:20pm **SA+AS+HC+SS-ThA1 Revealing Structure-Function Correlations in Fuel-Cells and Batteries.***,* ***Klaus Attenkofer****, E. Stavitski, M. Liu, D. Lu, M. Topsakal, D.J. Stacchiola, M.S. Hybertsen,* Brookhaven National Laboratory **INVITED**

To reveal the structure and even more important, the structure-function correlation of materials are essential prerequisites to the optimization and rational design of materials in energy storage and conversion applications. The complex processes resulting in the function typically involve not only the initial chemical reaction but a wide range of reorganizations, phase transitions, and transport phenomena which finally determine the efficiency of the material and its reliability in applications. The characterization challenge of visualizing changes on multiple length scales of ordered and disordered materials is one aspect of the characterization problem; to correlate the identified changes with the function of the material and distinguish the essential changes from other non-correlated alternation is the second equally important task.

In the talk we will show on various examples from the field of fuel cells and batteries, how high throughput hard X-ray spectroscopy can be combined with data analytics and theory to reveal the atomic structure of the ordered and disordered materials. In a next step a true imaging tool like transmission electron microscopy is used to verify this structure. The high throughput aspect of this approach provides not only a new opportunity to use database approaches to guarantee an unbiased method for the structure identification and optimization with a “field of view” in the nanometer range but also provides a new strategy to use data analytics, especially data mining approaches, to establish the structure-function correlation. The combination of ex-situ and operando experiments provides a statistical relevant data quantity and a diversity of the data necessary to this approach and is minimizing at the same time challenges caused by sample damage.

3:00pm **SA+AS+HC+SS-ThA3 Soft X-ray Spectroscopy for High Pressure Liquid***,* ***Ruimin Qiao****, J.-H. Guo, W. Chao,* Lawrence Berkeley National Laboratory **INVITED**

Soft X-ray spectroscopy (~50-1500eV), including both X-ray absorption and emission, is a powerful tool to study the electronic structure of various energy materials. Its energy range covers the K-edge of low-Z elements (e.g. C, N, O and F) and the L-edge of transition metal. Important information such as chemical valence, charge transfer and different ligand field could be directly extracted from the spectra. However, its application has been largely limited in materials that could be placed in vacuum (such as solid, below-ambient-pressure gas and liquid) because of the short penetration depth of soft x-ray. In this presentation, I will talk about the recent development of soft x-ray spectroscopy for high pressure liquid(up to 400 bars) at Advanced Light Source in Lawrence Berkeley National Lab.

4:00pm **SA+AS+HC+SS-ThA6 Surface Action Spectroscopy Using FHI FEL Infrared Radiation***,* ***Zongfang Wu****, H. Kuhlenbeck, W. Schöllkopf, H.J. Freund,* Fritz-Haber Institute of the Max Planck Society, Germany

In model catalysis and general surface science studies, the vibrational characterization of a surface is usually performed with HREELS (high-resolution electron energy loss spectroscopy) or IRAS (infrared reflection absorption spectroscopy). Both methods have disadvantages: HREELS suffers from its low resolution and (in the case of ionic samples) the presence of intense multiple phonon losses, while IRAS requires normalization of the spectrum with the spectrum of a reference sample, which leads to a contamination of the spectrum with features of the reference sample. Action spectroscopy with rare-gas messenger atoms [A. Fielicke et al., Phys. Rev. Lett. 93, 023401 (2004)] is an established method for vibrational spectroscopy of gas-phase clusters that avoids these disadvantages. Rare-gas atoms attached to gas-phase clusters may desorb when the incident infrared (IR) radiation is in resonance with a cluster vibration. The fragmentation rate, as monitored with a mass spectrometer, represents a vibrational spectrum, which can be used to draw conclusions regarding the cluster structure. Clusters, in this case deposited on a surface, are also highly relevant in model catalysis since they greatly influence catalytic reaction paths of supported catalysts. Both cluster shape and size matter. With this topic in mind a new apparatus for the application of IR FEL radiation to action spectroscopy of solid surfaces was set up at the Fritz Haber Institute (FHI), the V_2O_3(0001)/Au(111) (~10 nm thick) and a TiO_2(110) single crystal surface were studied as first test systems. The machine is connected to the FHI FEL, which is able to provide intense and widely tunable (3 – 60 µm) IR radiation. For V_2O_3(0001)/Au(111) the well-characterized vanadyl surface vibration and other surface vibrations could be detected, while bulk states turned out to be invisible to the method. Presumably, anharmonic vibrational coupling between the primary excited vibration and the rare-gas vs. surface vibration leads to desorption. This explains the surface sensitivity of the method as well as its insensitivity to bulk vibrations. In the case of the TiO_2(110) single crystal also rare-gas desorption resulting from an IR induced increase of the crystal temperature could be observed. This led to a better understanding of polaritons in rutile.

4:20pm **SA+AS+HC+SS-ThA7 Spectroscopic Insight into Resistive Switching Processes in Oxides***, C. Baeumer, C. Schmitz,* Forschungszentrum Juelich GmbH, Germany*; A. Kindsmüller,* RWTH Aachen University, Germany*; N. Raab, V. Feyer, D.N. Mueller, J. Hackl, S. Nemsak,* Forschungszentrum Juelich GmbH, Germany*; O.T. Mentes, A. Locatelli,* Elettra-Sincrotrone Trieste, Italy*; R. Waser, R. Dittmann,* ***Claus Michael Schneider,*** Forschungszentrum Juelich GmbH, Germany

Nonvolatile memories play an increasing role in modern nanoelectronics. Among the various storage concepts, resistive switching promises a high scalability. In oxides, the physical mechanism behind resistive switching involves electrically controlled local redox processes, which result in the formation and migration of oxygen vacancies. We studied these redox processes and their influence on the resistive switching in the model systems $SrTiO_3$(STO) and $ZrO_2$with a full suite of synchrotron-radiation based spectroscopy techniques. The resistive switching in STO proceeds via the growth of nanoscale conductive filaments, which poses considerable challenges to the spectroscopic characterization. Employing nanospectroscopy in an *operando* configuration we could unanimously relate the conductivity changes between the ON (low resistance) and OFF states (high resistance) to the redox-induced changes of the valencies and the formation of oxygen vacancies [1,2]. The retention time of the ON state in STO is determined by a reoxidation of the previously oxygen-deficient region and can be controlled by inserting an oxygen diffusion barrier. With respect to the reproducibility of the switching process, we find that the individual switching event is governed by a competition within a network of subfilaments, which has been created in the initial forming step. Upon resistive switching, one of these subfilaments becomes the current-carrying filament. However, during repeated switching the different subfilaments may become active, resulting in a cycle-to-cycle variation of the location and shape of the current-carrying filament, which determines the low-resistance state [3].

[1] C. Baeumer, C. Schmitz, A. Marchewka, D. N. Mueller, R. Valenta, J. Hackl, N. Raab, S. P. Rogers, M. I. Khan, S. Nemsak, M. Shim, S. Menzel, C. M. Schneider, R. Waser and R. Dittmann, Nat Commun **7** (2016) 12398.

[2] A. Kindsmüller, C. Schmitz, C. Wiemann, K. Skaja, D. J. Wouters, R. Waser, C. M. Schneider and R. Dittmann, APL Materials **6** (2018) 046106.

[3] C. Baeumer, R. Valenta, C. Schmitz, A. Locatelli, T. O. Mentes, S. P. Rogers, A. Sala, N. Raab, S. Nemsak, M. Shim, C. M. Schneider, S. Menzel, R. Waser and R. Dittmann, ACS Nano **11** (2017) 692.

4:40pm **SA+AS+HC+SS-ThA8 Visualizing Electronic Structures of Topological Quantum Materials by Synchrotron Based Photoemission Spectroscopy***,* ***Yulin Chen,*** Oxford University, UK **INVITED**

The electronic structure of matter is critical information that determine its electric, magnetic and optical properties. The precise understanding of such information will not only help understand the rich properties and physical phenomena of quantum materials, but also guide the design of their potential applications.

Angle-resolved photoemission spectroscopy (ARPES) is an effective method in determining the electronic structures of materials: with its energy and momentum resolution, ARPES can directly map out dispersions of electronic bands in the reciprocal space with critical parameters (such as the energy gap and width of bands, carrier type, density and the Fermi-velocity, etc.).

In this talk, I will first give a brief introduction to this powerful experimental technique, its basic principle and the rich information it can yield by using synchrotron radiation light source, then focus on its recent application to topological quantum materials (including some of our works on topological insulators, Dirac and Weyl semimetals [1]). Finally, I will review the recent development in ARPES and give a perspective on its future directions and applications.

[1] Science, 325, 178 (2009), Science, 329, 659 (2010), Nature Nanotechnology, 6, 705 (2011), Nature Chemistry, 4, 281 (2012), Nature Physics, 9, 704 (2013), Science, 343, 864 (2014), Nature Materials, 13, 677 (2014), Nature Physics, 11, 728 (2015), Nature Materials, 15, 27(2016), Nature Communications 7, 12924 (2016), Nature Communications, 8, 13973 (2017).

5:20pm **SA+AS+HC+SS-ThA10 Electronic Structure of FeO, γ-Fe_2O_3 and Fe_3O_4 Epitaxial Films using High-energy Spectroscopies***,* ***German Rafael Castro,*** Spanich CRG BM25-SpLine Beamline at the ESRF,, France*; J. Rubio Zuazo,* Spanish CRG BM25-SpLine at the ESRF, France*; A. Chainani,* Condensed Matter Physics Group, NSRRC, Taiwan, Republic of China*; M. Taguchi,* RIKEN SPring-8 centre, Japan*; D. Malterre,* Institut Jean Lamour, Universite de Lorraine, France*; A. Serrano Rubio,* Spanich CRG BM25-SpLine Beamline at the ESRF, France

Today, one of the materials science goals is the production of novel materials with specific and controlled properties. Material composites, which combine different materials, with specific and defined properties, mostly of multilayer thin films, are a promising way to create products with specific properties, and, in general different of those of the constituents. The chemical, mechanical, electric and magnetic properties of such materials are often intimately related to their structure, composition profile and morphology. Thus, it is crucial to yield with an experimental set-up capable to investigate different aspects related with the electronic and geometric structure under identical experimental conditions, and, in particular, to differentiate between surface and bulk properties. There are few techniques able to provide an accurate insight of what is happening at these interfaces, which in general are buried by several tens of nanometres inside the material. The Spline beamline Branch B at the ESRF, the European Synchrotron, offers unique capabilities in this respect.

In this contribution we will present the study of the electronic structure of well-characterized epitaxial films of FeO (wustite), γ-Fe_2O_3 (maghemite) and Fe_3O_4 (magnetite) using Hard X-ray Photoelectron Spectroscopy (HAXPES), X-ray Absorption Near Edge spectroscopy (XANES) and electron energy loss spectroscopy (EELS). We carry out HAXPES with incident photon energies of 12 and 15 keV in order to probe the bulk-sensitive Fe 1s and Fe 2p core level spectra. Fe K-edge XANES is used to characterize and confirm the Fe valence states of FeO, γ-Fe_2O_3 and Fe_3O_4 films. EELS is used to identify the bulk plasmon loss features. A comparison of the HAXPES results with model calculations for an MO6 cluster provides us with microscopic electronic structure parameters such as the on-site Coulomb energy U_{dd}, the charge-transfer energy Δ, and the metal-ligand hybridization strength V. The results also provide estimates for the ground state and final state contributions in terms of the d^n, d^{n+1}L1 and d^{n+2}L2 configurations. Both FeO and γ-Fe2O3 can be described as charge-transfer insulators in the Zaanen-Sawatzky-Allen picture with $U_{dd} > \Delta$, consistent with earlier works. However, the MO6 cluster calculations do not reproduce an extra satellite observed in Fe 1s spectra of γ-Fe_2O_3 and Fe_3O_4. Based on simplified calculations using an M2O7 cluster with renormalized parameters, it is suggested that non-local screening plays an important role in explaining the two satellites observed in the Fe 1s core level HAXPES spectra of γ-Fe_2O_3 and Fe_3O_4.

5:40pm **SA+AS+HC+SS-ThA11 Single-Bunch Imaging of Detonation Fronts Using Scattered Synchrotron Radiation***, M.H. Nielsen, J.A. Hammons, M. Bagge-Hansen, L.M. Lauderbach, R. Hodgin, K. Champley, W. Shaw,* Lawrence Livermore National Laboratory*; N. Sinclair,* Washington State University*;* ***Trevor Willey,*** Lawrence Livermore National Laboratory

Radiographic imaging using a series of single pulses from synchrotron storage rings or x-ray free-electron lasers gives new insight into dynamic phenomena. One limitation of these sources is that the native and natural beam size at most end-station hutches is, at best, of mm-scale dimensions. Here, we describe a method for collecting full-field, radiographic images of cm-scale phenomena using focused pink-beam and scattering the x-rays, effectively creating point-source images. Although currently photon starved and highly dependent on parameters chosen (such as source-to-object and source-to-detector distances, scattering material, etc.) we are continuously improving the technique. At the Dynamic Compression Sector at the Advanced Photon Source, we use this capability to image detonation phenomena, particularly direct imaging of detonator performance, imaging initiation and run-up to detonation, imaging differences in ideal vs. non-ideal explosives, and have a goal to determining density during detonation at 10's of microns in resolution. In this presentation, we summarize our progress developing and using this technique in creating movies of dynamic phenomena as fast as 153.4 ns between frames, and as a method for imaging samples prior to, for example, collecting dynamic small-angle x-ray scattering or diffraction to observe nanodiamond growth kinetics and composition evolution during detonation.

Surface Science Division
Room 203C - Session SS+AS+BI+MI+NS-ThA

Organic/Inorganic Surfaces, Interfaces and Nanostructures

Moderator: Denis Potapenko, Princeton University

2:20pm **SS+AS+BI+MI+NS-ThA1 Investigation of the Stability of Ag Monolayers on Au(111) as a Function of Metal Adatom Diffusion**, *J.A. Phillips, L.K. Harville, H.R. Morgan, L.E. Jackson, G. LeBlanc,* ***Erin Iski***, University of Tulsa

The formation of an atomically thin, Ag layer on a Au(111) surface has been shown to significantly alter the thermal 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 metal systems as well as the adsorption of molecules on metals. EC-STM is a unique technique that, in addition to providing a local probe of the atomic surface structure, 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. The two sources of silver used for the Underpotential Deposition (UPD) process on Au(111) result in significantly different thermal stabilities of the surface. An important question is whether this stability can extend beyond thermal properties, which will be probed using the assembly of amino acids on Ag/Au(111). Using both EC-STM and UHV-STM (ultra-high vacuum STM), it has been shown that amino acids assist in the immobilization of diffusing adatoms on the surface and in the subsequent formation of metal islands (2). Since the molecular deposition in both cases takes place at room temperature, the current understanding is that the atoms on the surface are a function of the temperature of the surface and are not pulled out of the surface itself. Importantly, these systems provide a unique glimpse into metal surface diffusion and offer the ability to study the mass transport of metal atoms. This study focuses on how an application of the thin Ag film on the Au(111) will disrupt or assist in the metal adatom transport and whether the known thermal stability can extend to other surface properties, thus making the afforded stability more general. The interaction of the amino acids with the Ag films deposited at the two different potentials and the associated mass transport as measured by the size of metal islands on the surface will shed light on the stabilities of the two types of Ag layers. The ability to experimentally choose different surface properties based on electrochemical parameters and solution composition during metal deposition could lead to exciting new directions for thin film technologies.

(1) Iski *et al.* Electrochimica Acta (**2011**), 56, 1652-1661.

(2) Iski *et al. submitted to Communication Chemistry, May 2018.*

2:40pm **SS+AS+BI+MI+NS-ThA2 Chain-Length Dependent Reactivity of Thiolate Self-Assembled Monolayers with Atomic Gas Species**, ***Jeffrey Sayler***, *S. Brown, S.J. Sibener,* University of Chicago

Thiolate self-assembled monolayers (SAMs) provide platforms for easily customizable organic interfaces, making them an excellent model system for studying the chemical properties of organic thin films. In particular, their reactions with atomic gas species such as hydrogen and oxygen yield important information about gas-surface interactions in organic films, how static and dynamic disorder influence passivation, as well as various hydrogenation and oxidation reactions. We are currently investigating the reactions of these SAMs with atomic hydrogen (H), using an angle-directed atomic gas source and *in situ* ultra-high vacuum scanning tunneling microscopy (UHV-STM). First, a series of alkanethiolate SAM samples of varying chain length (8 to 11 carbon atoms long) were reacted with H, resulting in the monolayers' conversion from close-packed standing-up phase to lower density lying-down phase. Regardless of chain length or even-/oddness, which were expected to impact the effectiveness of H penetration into the monolayer due to differences in the chains' lateral mobility and terminal structure, all samples exhibited common kinetic mechanistic details. The relative reaction rates of different chain lengths were obtained using simultaneous dosing of multiple samples. Second, a close-packed 1H,1H,2H,2H-perfluorodecanethiol SAM (a fluorinated analog of the 1-decanethiol SAM) was reacted with H. Dosing this sample under the same conditions as the 1-decanethiol sample revealed little to no reactivity. Ongoing studies continue to explore the reactivity of this family of saturated SAM systems including investigation of the kinetics and mechanism of the lying-down phase's reactivity with H. Further investigations involving atomic oxygen and different SAM chemical compositions and structures will follow.

3:00pm **SS+AS+BI+MI+NS-ThA3 Scan Probe Studies of Lithium Transfer through Solid State Electrochemical Interfaces**, ***Janice Reutt-Robey***, University of Maryland College Park **INVITED**

All solid-state electrical energy storage devices are of immense interest as safer alternatives to those based upon flammable liquid electrolytes. Understanding the rates and elementary processes for lithium ion transport through anode-solid electrolyte-cathode interfaces is essential, but obscured by heterogeneous samples and unknown local potentials. I will present new nanoscale studies of lithiation/delithiation across well-defined interfaces created with actuated nanobattery junctions. Conventional STM metallic tips, clad with a thin film of electrode material ($LiCoO_2$ or Li) and a capping film of solid electrolyte ($Li_xAl_2O_3$ or Li_20), function as ½ cells. Probes are positioned and electrochemically cycled at singular surfaces of model electrodes – Si(111), Si(100), C(0001). At the nanoscale, hysteresis in charging/discharging is monitored as a function of interface structure and materials properties. UHV measurements preserve the chemical integrity of the material interfaces and allow traditional (cyclic voltammetry, stepped potential) and nontraditional (stepped stress) electrochemical measurements to separate electron/ion contributions to charge transfer. The data reveal how induced variations in local lithium concentration impact rates for charging/discharging and contribute to hysteretic behavior. Further, stress-induced current transients show non-Cotrellian time behavior, attributed to a lithium ion concentration gradient in the solid electrolyte. Modeling of nanobattery data allows for testable predictions of material properties. Finally we show how "inverted" Scanning Tunneling Spectroscopy provides a useful tool to characterize the electrical band gap of the tip 1/2 cell materials, while imaging reveals the distribution pattern of lithium ions at the cycled electrode surfaces.

This work was supported as part of the Nanostructures for Electrical Energy Storage (NEES), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award number DESC0001160.

4:00pm **SS+AS+BI+MI+NS-ThA6 Adsorption and Self-assembly of Halogenated Organic Molecules on the Si(111) √3×√3-Ag Surface**, ***Renjie Liu***, Lakehead University, Canada; *C. Fu, A.G. Moisseev, M.R. Rao, Y. Chen, D.F. Perepichka,* McGill University, Canada; *M.C. Gallagher,* Lakehead University, Canada

Given potential applications in molecular electronics, organic thin films continue to attract a great deal of scientific attention. Furthermore, organic-inorganic semiconductor hybrids have been identified as a possible platform for future devices. Generally such a device would require thin films of functionalized organic molecules grown on silicon surfaces. To promote the growth of high quality films, the Si surface needs to be passivated. For example, the Si(111) √3×√3-Ag surface has been shown to be weakly interacting, allowing molecules to remain mobile and form well ordered layers [1].

In this work we compare the adsorption and self-assembly of two halogenated molecules of threefold symmetry; 2,4,6-tris(4-iodophenyl)-1,3,5-triazine (TIPT), and tribromotrioxaazatriangulene (TBTANG) on the Si(111)-√3×√3-Ag surface. The self assembly of TIPT on HOPG and Au(111) has been reported previously [2], and heteroatom forms of triangulene are of particular interest in molecular electronics [3].

We find that both molecules display high mobility on the √3-Ag surface. With increasing molecular dose, TIPT forms supramolecular domains defined by a 2.0 nm by 1.8 nm rectangular cell. The size and symmetry of the unit cell provides strong evidence that a large fraction of the monomers do not undergo de-halogenation, and that the dominant interaction within the domains is intermolecular I···H hydrogen-bonding. As the coverage approaches one monolayer, the film consists of supramolecular domains of limited extent separated by regions of disorder. STM images at lower coverage reveal that molecular adsorption increases the defect density of the underlying √3-Ag layer. We believe that a small fraction of the TIPT molecules de-iodinate on adsorption and that the iodine subsequently reacts with the Ag overlayer. The increased defect density limits the extent of the supramolecular domains on this surface.

In contrast, TBTANG exhibits long-range self-assembly of intact molecules. The ordered structure is characterized by several closely packed rows of molecules. Within the rows the repeating motif is two-molecules linked together by Br···Br interactions. With increasing coverage, the √3 surface remains unaffected and the self assembled layer extends over the entire surface.

[1] Yokoyama, T. *et al.*, *J Chem Phys* **142**, 204701 (2015).

[2] Gatti, R. *et al.*, *J. Phys. Chem. C* **118**, 25505–25516 (2014).

[3] Nakatsuka, S. *et al.*, *Angewandte Chemie* **129**, 5169–5172 (2017).

4:20pm **SS+AS+BI+MI+NS-ThA7 Electron Interactions with Alkanethiol Self-assembled Monolayers on Au(111)***, **Jodi Grzeskowiak**,* University at Albany-SUNY*; C.A. Ventrice, Jr.,* SUNY Polytechnic Institute

Self-assembled monolayers (SAMs) are often used for applications such as molecular electronics, selective deposition, and various forms of surface modification. Advanced lithography within the semiconductor industry is adopting ever shorter wavelengths of light such that the interaction of secondary electrons with the organic resist is becoming the primary mechanism for photo-initiated electro-chemical solubility changing reactions. In order to study the interaction of low energy electrons with thin organic films, measurements have been performed on electron decomposition of alkanethiol molecules grown on Au(111) substrates. SAMs have been grown via both solution and vapor phase methods. These monolayers arrange into two distinct phases commonly referred to as lying down and standing up. The lying down phase is a physisorbed layer that is only weakly interacting with the substrate via Van der Waals forces. Conversely, the standing up phase is a chemisorbed species that is more strongly bound to the substrate. Various surface analysis techniques were used to characterize the monolayers before and after electron exposure. Low energy electron diffraction (LEED) was used to determine the structure of the SAM and the rate of decomposition. Temperature programmed desorption (TPD) in combination with mass spectrometry was used to evaluate the thermal stability and bonding strength of the attached SAMs and the decomposition products from electron exposure.

4:40pm **SS+AS+BI+MI+NS-ThA8 Measuring the Electronic Properties of Organic Single Crystals***, **Sujitra Pookpanratana**, E.G. Bittle, C.A. Hacker, S.W. Robey,* National Institute of Standards and Technology (NIST)*; R. Ovsyannikov, E. Giangrisostomi,* Helmholtz-Zentrum Berlin, Germany

Organic and molecular-based compounds have found commercial application in consumer-based electronics. Organic semiconductors can be integrated onto device structures in different physical forms such as single crystals, polycrystalline thin-films, or amorphous thin-films. The structural order of the molecular solid profoundly influences the electronic properties, that in turn controls important properties, such as the transport gap and binding energy of the highest occupied molecular orbital (HOMO) [1, 2], that govern how an electronic device operates. Photoemission can play a vital role in illuminating these important electronic properties. While there are numerous photoemission spectroscopic measurements of organic semiconductors in thin-film structures, far fewer attempts have been made to determine the "fundamental" electronic properties for pristine organic single crystals.

Here, we present results of photoemission measurements for single crystalline (SC) dinaphthothienothiophene (DNTT). DNTT is a small molecule-based thienoacene and has demonstrated carrier mobilities approaching 10 $cm^2/(V\ s)$ [3], is air-stable [4] and durable against accelerated temperatures and humidity conditions.[5] While there are many device studies that establish DNTT and other related thienoacenes for a variety of applications, detailed electronic and chemical structure studies are lacking. Electronic "band" structure measurements using a novel angle-resolved time-of-flight electron spectrometer is performed on SC-DNTT, and multiple highest occupied molecular orbitals are resolved of varying widths. Modest dispersion of the frontier HOMO is observed, and this result will be discussed in context of the charge carrier behavior of DNTT reported in the literature.

[1] J. Ivanco et al., Adv. Mater. 15, 1812 (2003)

[2] S. Krause et al., Org. Electron. 14, 584 (2013)

[3] W. Xie et al., Adv. Mater. 25, 3478 (2013)

[4] U. Zschieschang et al., Adv. Mater. 22, 982 (2010)

[5] N. K. Za'aba et al., Org. Electron. 45, 174 (2017)

5:00pm **SS+AS+BI+MI+NS-ThA9 Surface Functionalization of Porous Substrates via Initiated Chemical Vapor Deposition***, **Christine Cheng**, M. Gupta,* University of Southern California

Porous materials are used in various applications including separation membranes, paper-based microfluidics, and flexible electronics. Tuning surface properties of porous materials enhances the versatility of existing materials, giving them new functions and applications. However, traditional surface modification methods are typically solvent-based, which limits the range of substrates that can be coated. In this work, initiated chemical vapor deposition was used to continuously modify the surface of large areas of porous substrates in an all-dry vacuum process. A superhydrophobic polymer was deposited onto a porous substrate and the coating was characterized using contact angle goniometry, X-ray photoelectron spectroscopy, and scanning electron microscopy to study the uniformity of the coating along the entirety of the substrate. The superhyodrophobicty of the coated porous substrate is attributed to the deposited polymer and the roughness of the substrate. Addition of a perfluorinated liquid to the superhydrophobic porous substrate formed a slippery liquid-infused porous surface. A hydrophilic polymer was deposited on top of the superhydrophobic polymer to demonstrate the facile stacking of polymer layers with different chemistries using this process.

5:20pm **SS+AS+BI+MI+NS-ThA10 Atomic-Scale Understanding of Anatase Nanocatalyst Activation***, **William DeBenedetti**[1], E.S. Skibinski, M.A. Hines,* Cornell University

Our ability to predict the chemical reactivity of nanocatalysts has been stymied by our lack of atomic-scale understanding of nanocatalyst surface structure. Specifically, do nanocatalyst surfaces adopt a bulk-terminated structure or do they reconstruct to minimize their surface free energy, thereby lowering their chemical reactivity as observed in ultra-high vacuum? Furthermore, do nanocatalysts processed at higher temperature maintain their low-chemical-reactivity, reconstructed surfaces when used at low temperatures and under typical operating conditions?

Using a new technique for the growth of highly aligned anatase (001) nanocatalysts, we will show that solution-synthesized anatase is terminated by a monolayer of fluorine, which acts as an atomic-scale protective coating against adventitious contamination. We will also show that carboxylic acid solutions, the most common TiO_2 functionalization chemistry, causes a spontaneous reorganization of a reconstructed nanocatalyst, leading to a five-fold increase in the number of reactive sites. This surface reorganization is not observed when carboxylic acids are dosed from the gas phase, indicating that experiments in ultra-high vacuum environments lead to trapped states that may not be relevant to nanocatalysts in ambient conditions. *Ab initio* calculations show that although the carboxylic acid termination is slightly less effective at removing surface stress than the reconstructed surface, it is more effective in lowering the surface free energy. These findings suggest that bulk-terminated metal oxide nanocatalysts may be common under ambient operating environments, even after high-temperature processing or if reactants are rinsed off.

5:40pm **SS+AS+BI+MI+NS-ThA11 Mechanistic view of Solid-Electrolyte Interphase Layer Evolution at Li-metal Anode***, **Venkateshkumar Prabhakaran**,* Physical Sciences Division, Pacific Northwest National Laboratory*; M.H. Engelhard, A. Martinez,* Environmental Molecular Science Laboratory, Pacific Northwest National Laboratory*; G.E. Johnson,* Physical Sciences Division, Pacific Northwest National Laboratory*; S. Thevuthasan,* Environmental Molecular Science Laboratory, Pacific Northwest National Laboratory*; V. Murugesan,* Physical Sciences Division, Pacific Northwest National Laboratory

A molecular-level understanding of structural and chemical transformations of electrolyte at solid-electrolyte interfaces (SEI) is critical for rational design of electrochemical materials. Despite numerous studies, evolution of the transient and metastable species which dictates the cascade of interfacial reactions are still not clear. The challenge is to establish the chemical homogeneity within interface to clearly delineate the origin of various decomposition reaction products and their energetic pathways. Soft landing of mass-selected ions is ideally suited for building the interface with selected constituent which can alleviate the complexity

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[1] **National Student Award Finalist**

associated with diverse and correlated processes within SEI layer.[1-4] Herein, we report the development and first demonstration of new capabilities that combine ion soft landing with *operando* infrared reflection-absorption spectroscopy (IRRAS) to study the decomposition of counter anions and solvent molecules on bare lithium metal surfaces. Specifically, we discreetly deposited sulfonyl imide based electrolyte anion (TFSI$^-$) and solvated Lithium cations without corresponding counter ions onto bare lithium metal using soft landing approach and monitored their decomposition using *in-situ* IRRAS and *ex-situ* x-ray photoelectron spectroscopy (XPS). *Operando* IRRAS and XPS measurements captured the signatures of transient species arising from decomposition of electrolyte anions and solvent molecules in real time. We will discuss, our unique approach of building interface with precise control over the constituents and subsequently detect the spectroscopic signatures of transient species during decomposition processes.

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Thin Films Division
Room 104B - Session TF+AS+EL+EM+NS+PS+SS-ThA

IoT Session: Thin Films for Flexible Electronics and IoT

Moderators: Jesse Jur, North Carolina State University, Siamak Nejati, University of Nebraska-Lincoln

2:20pm **TF+AS+EL+EM+NS+PS+SS-ThA1 Ultraflexible Organic Electronics for Bio-medical Applications***, **Tomoyuki Yokota**, T. Someya,* The University of Tokyo, Japan **INVITED**

Recently, flexible electronics has much attracted to realize bio medical application for their flexibility and conformability [1-3]. To improve these characteristics, reducing the thickness of the device is very effective [4]. We have developed ultra-flexible and lightweight organic electronics and photonics devices with few micron substrates. We fabricated the 2-V operational organic transistor and circuits which has very thin gate dielectric layers. The gate dielectrics were composed of thin aluminium oxide layer and self-assembled monolayers (SAMs). Due to the very thin substrate and neutral position, our device shows the highly flexibility and conformability. The device doesn't be broken after crumpling.

And also we fabricated highly efficient, ultra-flexible, air-stable, three-color, polymer light-emitting diodes (PLEDs) have been manufactured on one-micrometer-thick parylene substrates. The total thickness of the devices, including the substrate and encapsulation layer, is only three micrometers, which is one order of magnitude thinner than the epidermal layer of the human skin. The PLEDs are directly laminated on the surface of skin and are used as indicators/displays owing to their amazing conformability as their superthin characteristics. Three-color PLEDs exhibit a high external quantum efficiency (EQE) (12, 14, and 6% for red, green and blue, respectively) and large luminescence (over 10,000 candelas per square meter at 10 V). The PLEDs are integrated with organic photodetectors and are used as pulse oximeter.

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3:00pm **TF+AS+EL+EM+NS+PS+SS-ThA3 Molecular Surface Chemistry for Improved Interfaces in Organic Electronics***, **Jacob W. Ciszek**,* Loyola University Chicago

Organic optoelectronic devices (OLED, OFETs, etc.) contain at least one, if not multiple instances of overlayers deposited onto organic semiconductors. The generated interface is inherently flawed with issues such as non-ohmic contact, overlayer delamination, or deposition induced damage arising. Traditionally, this is addressed by physical vapor deposition of yet another layer or by reengineering the materials in the device stack. In contrast, a reaction based approach allows for a wider range of function to be installed via molecular components in an organized and oriented manner, all while take advantage the inherent reactivity of the organic molecules which comprise the semiconducting layer. We have developed this approach via a "click-like" Diels-Alder chemistry whereby prototypical acene films (tetracene or pentacene) can be appended with a variety of small molecules to form an interfacial layer only ~5 Å thick. This chemistry is then applied towards improving the metal on semiconductor contact. As a demonstration of principle, Diels-Alder chemistry is utilized to form covalent bonds linking the organic semiconductor with a deposited metal contact thereby eliminating the poor adhesion present in this system. Application of the chemistry towards contact potential shifts is presented, while work towards sensing applications concludes the talk.

3:20pm **TF+AS+EL+EM+NS+PS+SS-ThA4 Investigation of Low Temperature ALD-deposited SnO_2 Films Stability in a Microfabrication Environment***, **Tony Maindron**, S.M. Sandrez, N.V. Vaxelaire,* CEA/LETI-University Grenoble Alpes, France

For applications such as displays (LCD, OLED) or solar cells, it is mandatory to use Transparent Conductive Oxides (TCOs) so as to allow light to extract out of the circuit or for light harvesting, respectively. In display technology, TCOs are also studied so as to replace the silicon technology developed to make the semiconducting channel in thin-film transistors. The mainstream TCO today is indium tin oxide (ITO), (90% indium oxide and 10% tin oxide). It has the advantage of having a high conductivity and a low surface resistivity, of the order of 10 ohm/square, while having a transmittance greater than 85% over the entire visible spectrum. However, it has several drawbacks, including the scarcity of indium and the high cost associated to its extraction process, which has prompted the scientific community to look for alternative TCOs. Among all TCOs, ZnO has been widely studied as a low cost single-metal oxide alternative material to ITO, as well as its multi-metal oxide derivatives using a dedicated metal dopant to control its electrical conductivity, as for instance with Al (ZnO:Al or AZO). One issue however with ZnO films lays in their relative chemical stability to water. It has been shown that films of ZnO or AZO change their physical properties when exposed to moisture: electrical conductivity decreases, roughness can increase, and optical characteristics are modified. By extension, when ZnO-based TCOs have to be finely patterned by photolithography, their high sensitivity to water-based solutions can be a severe issue. In our laboratory, we have noticed that ZnO and AZO films made by ALD at 150 °C typically are not stable in a microfabrication process: a large decrease (~ 20 %) of AZO thickness after the development step of photoresists used to pattern the TCO film has been noticed. One way to stabilize ZnO-based compounds is to anneal the films at high temperatures. However for some dedicated applications that use fragile substrates (plastic films for flexible organic electronics for instance), such post annealing processes at high temperature (typ. > 150 °C) cannot be applied. An alternative is to explore alternative materials to AZO: we found out that SnO_2 ALD (150 °C) shows very promising features regarding the stability under a microfabrication environment, while having good electrical and optical characteristics.

4:00pm **TF+AS+EL+EM+NS+PS+SS-ThA6 Dopant Distribution in Atomic Layer Deposited ZnO:Al and In_2O_3:H Films Studied by Atom Probe Tomography and Transmission Electron Microscopy***, Y. Wu, B. Macco,* Eindhoven University of Technology, The Netherlands*; A.D. Giddings, T.J. Prosa, D.J. Larson,* CAMECA Instruments Inc.*; S. Kölling, P.M. Koenraad, F. Roozeboom, **Erwin Kessels**, M.A. Verheijen,* Eindhoven University of Technology, The Netherlands

Transparent conductive oxides (TCOs) are ubiquitous in many of today's electronic devices, including solar cells. Atomic layer deposition (ALD) is a promising method to prepare high quality TCO films due to its well-known virtues – i.e., precise growth control, excellent conformality and uniformity – combined with its damage-free character. Here we report on two types of TCO films that we have studied by a combination of atom probe tomography (APT) and high-resolution transmission electron microscopy (TEM). The aim was to get more insight into how the dopants are distributed in the films.

The first study was carried out on ZnO:Al prepared by alternating cycles of $Zn(C_2H_5)_2$ and H_2O with cycles of $Al(CH_3)_3$ and H_2O in a supercycle fashion at 250 ºC. For this material it is known that the maximum conductivity achievable is limited by the low doping efficiency of Al. To better understand the limiting factors for the doping efficiency, the 3-dimensional distribution of Al atoms in the ZnO host material matrix has been examined at the atomic scale by the aforementioned techniques [1]. Although the Al distribution in ZnO films prepared by so-called "ALD supercycles" is often presented as atomically flat δ-doped layers, in reality a broadening of the Al-dopant layers was observed with a full-width-half-maximum of ~2 nm. In addition, an enrichment of the Al at grain boundaries was seen.

The second study involved In_2O_3:H prepared by InCp and a mixture of O_2 and H_2O at 100 ºC. This material provides a record optoelectronic quality after post-deposition crystallization of the films at 200 ºC. Since both the H dopant incorporation and the film microstructure play a key role in determining the optoelectronic properties, both the crystal growth and the incorporation of H during this ALD process were studied [2]. TEM studies show that an amorphous-to-crystalline phase transition o ccurs in the low temperature regime (100-150 °C), which is accompanied by a strong decrease in carrier density and an increase in carrier mobility. Isotope studies using APT on films grown with D_2O show that the incorporated hydrogen mainly originates from the co-reactant and not from the InCp precursor. In addition, it was established that the incorporation of hydrogen decreased from ~4 at. % for amorphous films to ~2 at. % after the transition to crystalline films.

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4:20pm **TF+AS+EL+EM+NS+PS+SS-ThA7 Roll-to-Roll Processable OTFT Sensors and Amplifier***, **Kai Zhang**,* University of Oxford, Department of Materials, UK*; C.-M. Chen, B. Choubey, H.E. Assender,* University of Oxford, UK

The high flexibility and relatively low cost of organic electronics are gradually providing more possibility for their application. Compared with conventional silicon based electronics, organic electronics have relatively short lifecycles and processor speed, but they are more promising in the market of wearable and flexible devices, for example, wearable health care devices, simple memory devices and flexible displays. In recent years, some flexible and wearable sensors have been developed, e.g. skin-touching sensors embedded in a sports suit can detect the change of heart rate, blood pressure, ion concentration of perspiration, or infrared radiation from the human body.

In most sensors based on organic thin film transistors (OTFT) made to date, the semiconductors are employed directly to detect analytes. However, (1) the lifecycles of this design is short due to the low stability of organic semiconductors; and (2) any modification for selectivity needs to be compatible with the semiconductor.

In this paper, we present sensors based upon an extended floating gate in order to separate the sensory area from the semiconductor. Transistors are manufactured, using our roll-to-roll vacuum webcoating facility, using a high-throughput all evaporation process (Ding et al., 2016, Taylor et al., 2015). We have demonstrated the principle of operation of a floating gate sensor integrated with the vacuum-deposited OTFT, by means of a simple strain sensor, using ferroelectric PVDF on the extended floating gate to directly act as a sensory material. To amplify the sensor signal further, a series of current mirrors and differential amplifiers have been designed based on the properties of single OTFTs. The combination of organic amplifier and OTFT sensor will be helpful to transduce sensing signal to a suitable level for wireless signal reading from flexible devices.

Reference:

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4:40pm **TF+AS+EL+EM+NS+PS+SS-ThA8 Functionalization of Indium Gallium Zinc Oxide Surfaces for Transparent Biosensors***, X. Du, S. John, J. Bergevin, **Gregory Herman**,* Oregon State University

Amorphous indium gallium zinc oxide (IGZO) field effect transistors (FETs) are a promising technology for a wide range of electronic applications including implantable and wearable biosensors. We have recently evaluated the functionalization of IGZO back channel surfaces with a range of self-assembled monolayers (SAM) to precisely control surface chemistry and improve stability of the IGZO-FETs. The SAMs evaluated include, n-hexylphosphonic acid (n-HPA), (3,3,4,4,5,5,6,6,6-nonafluorohexyl) phosphonic acid (FPA), and (3-aminopropyl) trimethoxysilane (APTMS). A comparison of the surface chemistry is made for bare and SAM functionalized IGZO back channel surfaces using X-ray photoelectron spectroscopy and electronic device measurements in air and phosphate buffer solution (PBS). We find significantly improved device stability with the SAMs attached to the IGZO back channel surface, both in air and PBS. We related this to the reduction of traps at the back channel surface due to SAM passivation. To further evaluate the IGZO-FETs as biosensors we have immobilized glucose oxidase (GOx) to the APTMS functionalized IGZO back channel surface using glutaraldehyde. We find that both the FPA functionalized and the GOx immobilized surfaces are effective for the detection of glucose in PBS. Furthermore, the GOx immobilized IGZO-FET based glucose sensors have excellent selectivity to glucose, and can effectively minimize interference from acetaminophen/ascorbic acid. Finally, we will discuss fully transparent IGZO-FET based glucose sensors that have been fabricated directly on transparent catheters.These results suggest that IGZO-FETs may provide a means to integrate fully transparent, highly-sensitive sensors into contact lenses.

5:00pm **TF+AS+EL+EM+NS+PS+SS-ThA9 Large Area Atmospheric Pressure Spatial ALD of IZO and IGZO Thin-film Transistors***, C. Frijters, I. Katsouras, A. Illiberi, G. Gelinck,* Holst Centre / TNO, Netherlands*; **Paul Poodt**,* Holst Centre / TNO and SALDtech B.V., Netherlands

Atmospheric pressure Spatial ALD is able to deliver high deposition rates while maintaining the advantages of conventional ALD, such as low defect density, high conformality and thickness uniformity. An emerging application for Spatial ALD is flat panel (OLED) display manufacturing. Examples include oxide semiconductors and dielectric layers for use in thin-film transistors (TFT's), and thin-film encapsulation for flexible OLED displays. As today's displays are fabricated on glass plate sizes in the order of several square meters, a remaining challenge is the development of large-area Spatial ALD deposition technology that is able to combine high throughput with uniform performance across very large areas.

We are developing large area Spatial ALD technology, and as a first step between the lab and the display fab, we have installed a large area Spatial ALD sheet-to-sheet tool which can handle up to 400x325 mm^2 sized substrates. With this tool we are able to deposit uniform films across a deposition width of 400 mm and thickness non-uniformities of ~ 1%. The whole tool is operated under an atmospheric pressure but inert N_2 environment. The tool can be used to deposit a variety of materials using both thermal and plasma-enhanced Spatial ALD.

We will present about the fabrication and performance of 30 cm x 30 cm TFT backplanes with $InZnO_x$ (IZO) and $InGaZnO_x$ (IGZO) oxide semiconductors deposited by spatial ALD. The IZO and IGZO films were deposited by plasma enhanced Spatial ALD using co-injected In-, Ga- and Zn-precursors and an atmospheric pressure N_2/O_2 plasma. The deposition process has been optimized in terms of film composition and electrical properties on a lab-scale reactor before being translated to the large area spatial ALD rector. We will report on the yield and performance of the 30 cm x 30 cm TFT backplanes, including electrical properties such as the field effect mobility, V_{on} and bias stress stability and compare it with state-of-the-art sputtered IGZO TFT's. Finally, the challenges in up-scaling Spatial ALD to plate sizes of 1.5 m and beyond will be discussed.

5:20pm **TF+AS+EL+EM+NS+PS+SS-ThA10 Thin Film Ink-Jet Printing on Textiles for Flexible Electronics***, **Jesse Jur**, I. Kim, H. Shahariar,* North Carolina State University

Inkjet printing of thin film flexible electronics on textiles is an emerging field of research with advances in wearable technology. In this study we describe for the first-time a reliable and conformal inkjet printing process of printing particle free reactive silver ink on textile surfaces. Reactive silver ink is printed on fibers with eclectic polymers ranging from polyester and polyamide, and different structures of textiles such as knitted, woven, and nonwoven fabrics. The conductivity and the resolution of the inkjet-printed tracks are directly related to the fiber structures in the fabrics. Multiple passes of printing layers are needed to confirm the percolation of the metal network on porous, uneven surfaces. The conformity and the electrical conductivity of the inkjet-printed conductive coating on PET textiles are improved by in-situ heat curing the substrate during printing and surface modification, for example, by atmospheric oxygen plasma treatments. The in-situ heat curing potentially minimizes wicking of the ink into the textile structures. We have achieved the minimum sheet resistance of 0.2 Ohm/sq on polyester knit fabric, which is comparable to the conductive thick-paste used in the screen-printed process, as well as other traditional physical and chemical deposition processes on textile fabrics/yarns. Additionally, we have constructed textile knit structures which changes electric percolation depending on structural deformations of the knit loops, providing positive and negative gauge factors upon stretching. The printed patterns are post-treated with diluted silicone/UV curable aliphatic water-soluble polyurethane coating to improve the durability during washing. These findings open up the possibility of integrating inkjet printing in the scalable and automated manufacturing process for textile electronic applications.

5:40pm **TF+AS+EL+EM+NS+PS+SS-ThA11 Flexography Oil Patterning for In-line Metallization of Aluminium Electrodes onto Polymer Webs: Commercial Roll to Roll Manufacturing of Flexible and Wearable Electronics***, **Bryan Stuart**, T. Cosnahan, A.A.R. Watt, H.E. Assender,* University of Oxford, Department of Materials, UK

Vacuum metallisation of aluminium through shadow masks has been commercially used for decades for depositing electrodes on rigid semiconductor devices, however recent developments have enabled large area, continuous deposition of patterned metallization in the aesthetic printing industry and has the potential for electrode interconnects for devices on flexible substrates such as Polyethylene Terephthalate (PET) and Polyethylene Naphthalene (PEN). Flexible polymer webs of PET were coated (*SeeSupplementary Figure*) with 50 nm thick, 165 um wide aluminium electrodes by commercially compatible manufacturing at roll-to-roll web speed of 2.4 m min^{-1} showing tremendous potential for large scale manufacturing of wearable electronic devices in transistors, low level energy generation (Thermoelectric generators), energy storage (thin film batteries) or display technologies (LED displays) [1].

The in-line patterning process relies on adaptation of flexography ink printing which typically transfers ink to a rubber patterned plate for printing images onto polymer webs. The flexibility of the printing plate accommodates for irregularities in the surface of the substrate making this process desirable for large area manufacturing. Metallization has been used to deposit aluminium onto a flexography applied pattern by replacing ink with a low vapor pressure oil (e.g. Perfluropolyether, Krytox®). The radiative heating of aluminium metallization causes simultaneous evaporation of the oil pattern, thereby rapidly forming the desired metal pattern onto the un-patterned regions. Currently we are scaling-up the oil flexography/metallization process into an industrial-scale roll-to-roll coater with potential web widths of 350 mm and roll speeds of 100 m min^{-1}, in order to increase web speeds, and to expand the range of materials deposited and the functional devices to which they are applied.

This paper reports on in-line pattern deposition of aluminium and other materials as applied to functional devices, for example organic thin film transistors and thermoelectric devices. In particular we are able to demonstrate how the process can be compatible with other functional layers. We will report our studies of electrode precision (shapes/sizes) by patterned metallization and our first studies of sputtering with flexography patterning. The long term view is integration of this technology along the R2R production path for single pass/high speed production of low cost and flexible integrated circuits.

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Applied Surface Science Division
Room Hall B - Session AS-ThP
Applied Surface Science Division Poster Session

AS-ThP1 Toward an Improved Understanding of the role of soil organic matter in NOy cycling through Investigation of Heterogeneous Reactions with NO2+*, R. Hansen,* Indiana University*; **Mark Engelhard,*** Pacific Northwest National Laboratory*; J. Raff,* Indiana University

Molecular level investigation of compositional changes due to heterogeneous reactions of nitrogen oxides (NO_x, NO_y) with soil organic matter (SOM) is important to develop a fundamental scientific understanding of the soil/atmosphere interface. In addition, interactions between NO_x reservoir species and SOM play a more important role in NO_x and NO_y recycling than previously realized. Despite the importance of soil to the global terrestrial-atmospheric cycling of nitrogen, interactions of N_2O_5 with SOM are not well understood. Uncertainty in these processes is problematic because it means that NO_y is not properly represented in the Earth-systems models used for prediction and regulation. The ultimate objective of this study is to investigate the production of NO_y from the reaction of N_2O_5 with SOM and elucidate the mechanisms that return NO_y back to the atmosphere, where NO_y can contribute to aerosol and O_3 formation. In the initial phase of this study, we reacted SOM standards with NO_2^+ (produced from concentrated HNO_3), which is an intermediate in the heterogeneous reaction of N_2O_5 with SOM. We then characterized these reaction products using X-ray photoelectron spectroscopy (XPS). XPS was used to measure the nitrogen chemistry before and after reaction of SOM with NO_2^+. These results will be discussed along with the pros and cons using XPS to characterize SOM chemistry.

AS-ThP2 Measuring the Damage Depth and Recovery of PEMA Thin Films using Multiple Technique Analysis*, **William Sgammato**, R.E. Simpson,* Thermo Fisher Scientific, UK

Sputtering polymer surfaces with monatomic Ar ions is known to induce changes in the polymer chemistry. PEMA in particular, is a "self-sealing" polymer type which means during Ar^+ sputtering cross-linking occurs. The advantage of using Ar cluster ions is that such chemical changes are not induced. It has also been demonstrated that Ar^+_n ions can be used to remove the damage layer produced by Ar^+ ions, thus recovering the surface chemistry. In this investigation this ability to recover the polymer surface is used to measure the relative thickness of the damage layer produced by Ar^+ ions. To facilitate this other techniques were used for film thickness measurement and calibration. AFM was used to accurately measure the thickness of the PEMA film, this data was then used to calibrate a separate scale that was used to estimate the thickness based on the colour of the surface. As the colour of the surface is dependent only on the refractive index of the material, the angle of incidence of the incoming light and the thickness of the film, the measurements can produce a high accuracy thickness estimate to within ± 10 nm. The estimate of the original film thickness, made using the film colour, ~ 400 nm was in good agreement with the average thickness measured using AFM 398 nm.

The results of this investigation showed that the relative depth of damage induced by a 3 keV Ar^+ ion beam in a PEMA thin film was 245 ± 10 nm. Film thickness measurements were also used to calibrate Ar^+ and Ar^+_n etch rates which were calculated as 0.94 and 2.60 nm/s respectively. The low Ar^+ etch rate was an indication of sample cross-linking during etching.

AS-ThP3 Determination of Band Offsets in Semiconductor Heterostructures (2D/3D) by using XPS*, **Mohamed Hedhili**,* King Abdullah University of Science and Technology (KAUST), Core Labs, Saudi Arabia*; M. Tangi, P. Mishra, T.K. Ng, B. Janjua, C.C. Tseng,* Photonics Laboratory, King Abdullah University of Science and Technology (KAUST), Saudi Arabia*; D.H. Anjum,* King Abdullah University of Science and Technology (KAUST), Core Labs, Saudi Arabia*; M.S. Alias,* Photonics Laboratory, King Abdullah University of Science and Technology (KAUST), Saudi Arabia*; N. Wei,* King Abdullah University of Science and Technology (KAUST), Core Labs, Saudi Arabia*; L.J. Li,* Physical Sciences and Engineering Division, King Abdullah University of Science and Technology (KAUST), Saudi Arabia*; B.S. Ooi,* Photonics Laboratory, King Abdullah University of Science and Technology (KAUST), Saudi Arabia

Heterojunctions are generally formed at the interface of different energy-gap semiconductor materials due to their mismatching electron energies in the valence bands. The values of valence-band mismatches or offsets hold a great significance for the optoelectronics applications and hence their accurate determination is of paramount importance. High-resolution X-ray photoemission spectroscopy (HR-XPS) is proven to be a powerful way of measuring the valence band offsets in such semiconductor heterojunctions. In this report, we extend HR-XPS studies for such measurements to 2D/3D types of heterojunctions. These 2D/3D junctions are synthesized by combining 3D semiconductors (e.g. GaN or InAlN) with 2D semiconductors (e.g. WSe_2 or MoS_2). By performing an elaborate XPS analysis, we are able to show the type of heterojunctions formed by these semiconductor materials. For instance, we observed that the heterojunction of GaN with either MoS_2 or WSe_2 is of “Type-II”. Whereas, the junction of InAlN with MoS_2 is “type-I”. The presented HR-XPS results are both supported and corroborated by performing the analaysis of these samples with other techniques including atomic force microscopy, scanning transmission electron microscopy, micro-Raman, absorbance, and microphotoluminescence . The band alignment parameters determined here provide a route toward the integration of group III nitride semiconducting materials with transition metal dichalcogenides (TMDs) for designing and modeling of their heterojunction-based electronic and optoelectronic devices.

AS-ThP4 Multi-technique Characterization of Nanowire-based Catalysts and Electrodes*, **Sarah Zaccarine**, C. Ngo,* Colorado School of Mines*; S. Shulda, S. Mauger, S.M. Alia, K.C. Neyerlin, B.S. Pivovar,* National Renewable Energy Laboratory*; S. Pylypenko,* Colorado School of Mines

In response to the increasing anthropogenic impact on the environment, it is vital to implement sustainable solutions to meet global energy demands. Polymer electrolyte membrane fuel cells (PEMFCs) are a promising option but the sluggish oxygen reduction reaction at the cathode leads to issues with cost and efficiency. Pt nanoparticles supported on high surface area carbon (Pt/HSC) are commonly used but suffer performance losses and do not meet Department of Energy targets for durability or cost. Extended surface nanostructures are a promising alternative as they show improved specific activity and durability. We have developed extended surface nanowire-based platinum nickel catalysts with durability, mass activity, and specific activity superior to Pt/HSC. Since the catalyst functions differently under altered conditions, it is crucial to study the catalyst at all stages as it transitions from a powder to a membrane electrode assembly (MEA), which requires a multi-technique approach.

The catalyst was studied as a powder, ink, fresh MEA, and tested MEA to determine the changes that occur as the catalyst is integrated into a full MEA. Several spectroscopy and microscopy techniques were utilized to address all relevant length scales (from atomic to micrometers). First, the catalyst was investigated using a combination of extended x-ray absorption fine structure (EXAFS) spectroscopy, x-ray photoelectron spectroscopy (XPS), scanning transmission electron microscopy (STEM) with energy dispersive x-ray spectroscopy (EDS) hypermapping, and atom probe tomography (APT) to obtain detailed information about distribution of platinum and nickel, discerning differences between surface and bulk speciation at nanometer and sub-nanometer scale. This detailed information about surface speciation was then used to better understand oxygen adsorption behavior of these catalysts, investigated using near-ambient pressure XPS (nAP-XPS). Second, evolution of the catalyst and catalyst-ionomer interface when incorporated in an electrode were examined with STEM/EDS and x-ray tomography. These studies offer invaluable insight into structure-performance relationships of the nanowire-based catalysts and development of efficient electrodes.

AS-ThP6 Characterization of Laser-Treated Ti-6Al-4V-Surfaces*, **Harry Meyer**, D. Leonard, A. Sabau,* Oak Ridge National Laboratory

Lightweight Al, Mg, and Ti alloys are ubiquitous in aerospace and automotive applications. When these alloy materials are joined, either to similar or dissimilar materials, the chemical and physical state of the surface determines the quality of the bond. Methods for cleaning (chemical) and texturing (physical) metal alloy surfaces prior to joining or paining have traditionally relied on aggressive chemicals that are now considered environmentally unfriendly. Costs for adequately protecting of worker and protecting the environment are high enough that alternate surface processing methods are needed. During the last two years ORNL, began a systematic study of a unique laser processing method for both cleaning and texturing metal surface simultaneously. This novel surface treatment method uses 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. Preliminary results for the Al-alloy laser-based surface treatment process were reported last year at this conference. One of the primary findings for Al-alloy surfaces was the development of an enhanced oxide surface region. Influence of the enhanced oxide on both adhesive joining and corrosion protection are now underway. Recently, we have extended these laser-processing studies to Ti-6Al-V4 (Ti64) alloys, which are widely used in the aerospace industry. Ti64 alloy surfaces can be cleaned using high-energy laser pulses (nanoseconds to milliseconds range) and, as with the Al-alloys, is accomplished mainly by surface melting and ablation. Our method is non-contact, does not rely on surface abrasion and significantly reduces the chemical impact of commonly used solvents and detergents. The process being optimized at ORNL uses 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 Ti64-alloy surfaces. Results from scanning transmission electron microscopies, x-ray photoelectron spectroscopy, and contact angle measurements on as received and laser–treated commercial Ti64-alloy surfaces will be presented. This abstract has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy.

AS-ThP7 Cross-Sectional Mapping vs. Depth Profiling Analysis: Is the Choice Always Clear?, *Kathryn Lloyd*, *J.R. Marsh,* DuPont Corporate Center for Analytical Sciences

Differences in chemistry across monolithic or multi-layered films are often critical to product performance. Each component in a formulation serves a purpose. It is important to be able to monitor the integrity of multi-layered structures, the striation or migration of components, the enrichment of components at interfaces, and the formation of buried defects.

Approaches used to obtain this information can be broadly separated into cross-sectioning (combined with chemical mapping) and depth profiling (with or without chemical mapping). Cross-sectioning calls for more labor up front to prepare the samples – potting in epoxy; microtoming -- but the resulting cross-sectional surfaces are amenable to multiple chemical mapping techniques, such as Raman microprobe, secondary ion mapping, and Energy Dispersive Spectroscopy (SEM/EDS), all of which exhibit comparable lateral resolution (around 1 micron). Depth profiling requires little to no sample preparation and offers higher depth resolution (10s of nanometers).

To a large degree, film and/or layer thickness determine the approach pursued. Practical depth profiling historically has not extended much more than 10 microns into a surface. Thus, for multilayer films with thicknesses on the order of 25 microns or more, cross-sectioning has been preferred. This can present problems for surface chemical mapping techniques such as ToF-SIMS, when even cryo-microtoming can result in a thin overlayer of smeared epoxy components covering the surface.

The advent of new gas cluster ion beam (GCIB) sputter sources has not only enabled cross-sectional ToF-SIMS mapping analysis for layered and heterogeneous organic systems, but has also made the choice between cross-sectioning and depth profiling not as clear. GCIB depth profiling through organic or polymeric material can be very efficient, making the idea of profiling through 25 microns or more not as impractical as it once was.

This presentation will show examples of cross-sectional mapping analysis and sputter depth profiling, exploring which factors can influence the choice of approach and illustrating some of the trade-offs involved.

AS-ThP8 Investigation on Human Evidences using ToF-SIMS Combined with Advanced Matching Recognition, *T. Terlier,* Korea Institute of Science and Technology*; J. Lee, M. Kang,* ***Yeonhee Lee****,* Korea Institute of Science and Technology, Republic of Korea

The expansion of the use of forensic sciences requires to develop new techniques providing prompt and reliable information. In terms of chemical analysis, the useful information ranges from trace elements, e.g. the elemental detection of residues in a specimen, to molecular information, e.g. the identification of high mass molecules. Time-of-Flight Secondary Ion Mass Spectrometry is able to provide a detailed 3D view of the elemental and molecular composition of solid samples and has already been used previously to analyze inorganic, organic and biological specimens, showing its strong potential to retrieve more information from trace evidence than the traditional methods.

Several challenges still prevent a widespread application of ToF-SIMS to forensic analysis. Samples from the human body are the most commonly collected specimens and these samples are particularly challenging for analysis due to the variety of specimens, including hair, fingerprints, fingernails and lipstick, and the complexity of the samples that can contain blood, saliva and/or sweat. A common material to almost all of the human specimens is cosmetics, which can provide crucial information about an individual. Through analysis of five different types of cosmetics - hair styling products, lipstick, lotion, nail polish, and foundations, we have collected a large range of ToF-SIMS spectra and build a cosmetic database from these reference samples.

The characterization of different types of human evidences has been performed to illustrate the large range of the possibilities given by the ToF-SIMS. However, to identify the chemical composition of the cosmetic residues and to determine their origins, advanced methods of classification and discrimination need to be applied. For example using Principal Component Analysis, it was possible to identify the cosmetic residues present on hair cuticles and to discriminate the hair product applied from a list of 16 references. Nevertheless, quantitative analysis can be required for identifying the exact nature of the residues. Thus, a new method combining Matching Factor and decision tree has been developed. Fingerprint analysis has been performed to identify the traces of residues contained in the fingerprint, which have also highlighted the fingerprint's ridges. After PCA segmentation, the extracted mass spectrum from the residue's region has been evaluated using a new matching recognition method, which has clearly indicated the origin of the cosmetic product.

The development of matching recognition method and the analysis performed on the human evidences has demonstrated that the ToF-SIMS is a promising way to help the forensic investigations.

AS-ThP10 Wafer Bonding Between LiTaO3(100) and Alpha-quartz SiO2(100) via Low Temperature (<220°C) NanoBonding™ Using Surface Energy Modification, ***Brian Baker****, J. Kintz, A. Yano, N. Herbots,* Arizona State University*; W.-L. Lee,* Cactus Materials, Inc.*; S.R. Narayan, J.M. Day,* Arizona State University*; R. Islam,* Cactus Materials, Inc.*; Y. Watznabe,* TDC Coporation*; M. Koury, M. Johnson, R.J. Culbertson, M. Magnus,* Arizona State University

Wafer bonding is displacing heteroepitaxy in the manufacture of heterostructures, such as tandem solar cells and sensors. High costs and poor yields limit effective production of opto-electronic devices and sensors.

In this work, piezoelectric LiTaO3(100) and alpha-quartz SiO2(100) wafer bonding is investigated via NanoBonding™ near 300K [1,2]. NanoBonding™ generates molecular bonds between surfaces at the nanoscale over large interfacial domains, creating a 2D bonding interphase between the two materials. First, electron exchange is created between surfaces by engineering a key hydrophilic-hydrophobic surface pairs (via wet chemical processes, spin, vapor, or plasma etching). This method catalyzes electronic exchange and bonding by modifying native surfaces to a less stable state where electronic displacement is enhanced. Surface Energy Modification is measured via the surface total energy γT, and its three components γLW, γ+, γ-. These values are based on the Van Oss-Chaudury-Good (vOCG) theory, and using high resolution Three Liquid Contact Angle analysis. A key feature of Surface Energy Modification for NanoBonding™ is the creation of 2D precursor phases on surfaces. Next, for nanocontacting, the surface has to be planarized at the macro, micro, and nano scales. Last, NanoBonding™ activation can occur on contact and/or after thermal activation.

NanoBonding™ depends thus on the control of surface energy, planarity at three scales, and composition. γT can be computed from 3LCAA. The liquids used are 18 MO water, glycerin, and α-bromo-naphthalene (10 10 µL droplets). The average γT, across as received 4" LiTaO3 wafer is 43.3 ± 2 mJ/m2 (hydrophobic). However, the electron acceptor energy Y(-) can vary from 43 mJ/m2 to 23 mJ/m2 (~50% difference). Regions with low Y(-) (low electron transfer) do not bond while those high Y(-) do. This correlates directly with bonded interfacial regions visualized when LiTaO3 wafer is nano-contacted with 4" quartz wafers. In this way, 3LCAA can determine one cause of bonding failures.

Thermal activation (100 and 200°C) does not enhance bonding as significant thermal expansion causes mismatch fractures, interface delamination, or thermal decomposition due to the high mobility of Li ions.

In conclusion, thermally or plasma activated wafer bonding is clearly not optimal for wafer bonding LiTaO3. To Si-based materials, causing high fracture rates for LiTaO3 as well Li out diffusion. Instead, Nanobonding(TM) is more appropriate due to a reduced fracture or thermal decomposition chance.

Herbots N. et al. US Pat. No 9,018,077 (2015), US Pat. No 9,018,077 (2017)

Herbots N., Islam R., US Pat. Pending (2018), filed March 18, 2018

AS-ThP11 Structural, Morphological and Electrical Properties of Multilayer Sequentially Sputtered Nb_3Sn Films for Different Layer Thicknesses

Md. Nizam Sayeed, Old Dominion University; *U. Pudasaini,* College of William and Mary; *H. E. Elsayed-Ali,* Old Dominion University; *G. Eremeev,* Thomas Jefferson National Accelerator Facility

Nb_3Sn is an intermetallic compound of A15 crystal structure that has type II superconductivity. Due to higher critical temperature T_c = 18.1 K and upper critical magnetic field of up to 30 T, Nb_3Sn is considered as an alternative of niobium for Superconducting Radio Frequency (SRF) applications in particle accelerators. Nb_3Sn coating on the inner surface of niobium SRF cavities can be operated at 4.2 K, whereas standard niobium cavities are currently operated at 2 K and consequently reduce the operation cost. However, synthesis of Nb_3Sn is challenging due to the availability of other phases of niobium and tin (Nb_6Sn_5 and $NbSn_2$), which have poor superconducting properties. We have fabricated Nb_3Sn films on sapphire using multilayer sequential sputtering. Several thin layers of Nb and Sn were deposited repeatedly by magnetron sputtering and annealed afterward at 950 °C for 3 hours to form Nb_3Sn. We have varied the Nb and Sn layer thicknesses of the films and characterized their crystal structure by X-ray diffraction (XRD), surface morphology by scanning electron microscopy (SEM), surface topography by atomic force microscopy (AFM), film stoichiometry by energy dispersive X-ray spectroscopy (EDS). The films showed crystalline structures of Nb_3Sn only. T_c up to 17.63 K with sharp superconducting transition has been achieved.

Biomaterial Interfaces Division
Room 101B - Session BI+AS+NS-FrM

Characterization of Biological and Biomaterial Surfaces

Moderator: Bill Theilacker, Medtronic

8:20am **BI+AS+NS-FrM1 Novel Insights into Skin Biology and Permeation of Actives using ToF-SIMS and 3D OrbiSIMS.*, David Scurr,*** The University of Nottingham, UK **INVITED**

This work presents the use of mass spectrometry imaging (specifically ToF-SIMS and 3D OrbiSIMS) as an emerging tool for skin analysis, offering the ability to perform chemical histology and monitor the distribution of xenobiotic compounds, namely antibacterial, cosmetic and pharmaceutical agents. Both 2D and 3D spatial distribution profiles of analytes within skin are achievable for both topically applied compounds following permeation and inherent compounds present in native tissue. Data acquired using the 3D OrbiSIMS can identify a significant number of biological molecules, unavailable using ToF-SIMS, including subtle chemical variations within single skin strata and / or individual cells.

Individual tape stripped layers of human *stratum corneum*, both native and following application of a topical compound can be imaged using ToF-SIMS and 3D OrbiSIMS. The sensitivity of these techniques has also enabled the detection of analytes from native tape stripped samples highlighted differences in the lipid composition of the *stratum corneum* relating to both intrinsic and extrinsic aging effects[1]. In particular, a significant increase in the presence and a localised spatial distribution was observed for cholesterol sulfate, which has been shown to play a key role in desquamation.

In conducting an analysis of native *ex vivo* porcine tissue we were successfully able to detect and spatially map chemical biomarkers of both the *stratum corneum* and underlying epidermis. In addition, using a gas cluster ion beam (GCIB), the 3D distribution of analytes throughout the epidermis could be visualised for both pharmaceutical and cosmetic topical products following Franz cell experiments. These methods can be used to illustrate enhanced topical delivery, for example in the use of supramolecular gels encapsulating ascorbic acid and microneedles applied prior to the application of imiquimod used for cosmetic and pharmaceutical purposes respectively.

[1] Starr, Johnson, Wibawa, Marlow, Bell, Barrett & Scurr, *Anal. Chem*. **2016**, 88 (8), pp 4400–4408

9:00am **BI+AS+NS-FrM3 Multivariate Analysis of ToF-SIMS Data using Mass Segmented Data Matrices: Polymers and Biointerfaces***, R.M.T. Madiona,* La Trobe University, Australia*; N.G. Welch,* CSIRO Manufacturing, Australia*; D.A. Winkler,* La Trobe University, Australia*; J.A. Scoble,* CSIRO, Austalia*; B.W. Muir,* CSIRO, Australia*; **Paul Pigram**,* La Trobe University, Australia

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is continuously advancing. The data sets now being generated are growing dramatically in complexity and size. More sophisticated data analytical tools are required urgently for the efficient and effective analysis of these large, rich data sets. Standard approaches to multivariate analysis are being customised to decrease the human and computational resources required and provide a user-friendly identification of trends and features in large ToF-SIMS datasets.

We demonstrate the generation of very large ToF-SIMS data matrices using mass segmentation of spectral data in the range 0 – 500 m/z in intervals ranging from 0.01 m/z to 1 m/z. No peaks are selected and no peak overlaps are resolved. Sets of spectra are calibrated and normalized then segmented and assembled into data matrices. Manual processing is greatly reduced and the segmentation process is universal, avoiding the need to tailor or refine peak lists for difficult sample types or variants.

ToF-SIMS data for standard polymers (PET, PTFE, PMMA and LDPE) and for a group of polyamides are used to demonstrate the efficacy of this approach. The polymer types of differing composition are discriminated to a moderate extent using PCA. PCA fails for polymers of similar composition and for data sets incorporating significant random variance.

In contrast, artificial neural networks, in the form of self organising maps (SOMs) deliver an excellent outcome in classifying and clustering different and similar polymer types and for spectra from a single polymer type generated using different primary ions. This method offers great promise for the investigation of more complex bio-oriented systems.

9:20am **BI+AS+NS-FrM4 Can you dig it? ToF-SIMS Tissue Depth Profiling***, **Daniel Graham**, T.B. Angerer, L.J. Gamble,* University of Washington

ToF-SIMS has been shown to provide detailed chemical information about cells and tissues with excellent lateral resolution. This has enabled looking at the 2D chemical distribution of lipids and other biological molecules within tissues and cells. Since cells and tissues are three dimensional constructs, it is of interest to be able to characterize their chemical composition in 3D. With the use of gas cluster ion beams (GCIBs) ToF-SIMS can attain very fine z-resolution (<10 nm) in depth profiles, however the use of ToF-SIMS for 3D imaging of biological samples is limited. This is likely due to the complexity of the materials and artifacts often encountered because of the presence of salts. In this work we use ToF-SIMS 3D depth profiling to optimize accurate reconstruction of depth profiles of planarian worm cross-sections. For this, dual beam depth profiles with a 25 keV Bi3$^+$ liquid metal ion gun (LMIG) for imaging and 10 keV Argon 1000 clusters for sputtering were acquired using an Iontof 5 system. Data reconstruction was carried out using the NBToolbox (https://www.nb.uw.edu/mvsa/nbtoolbox) ZCorrectorGui. It is well known that due to the fixed angle to of the analysis beam, the sequential images taken at each layer of the profile shift as a function of depth. Adjusting the beam steering during data acquisition and image shifting post data acquisition are used to account for this image shifting and more accurately reconstruct a 3D representation of the data. Areas with distinct structural features were chosen for depth profiles in order to aid in ascertaining the accuracy of the 3D data reconstruction. These studies will help establish the viability of 3D data reconstruction of complex biological samples and could be instrumental in being able to localize chemical distributions throughout tissues and cells.

10:00am **BI+AS+NS-FrM6 Novel Insights into Drug Release by a Functionalized Biomaterial and Dispersion into Bone using Surface Analytical Techniques***, **Marcus Rohnke**, C. Kern, B. Mogwitz, S. Ray,* Justus-Liebig University Giessen, Germany*; J. Thomas,* IFW Dresden, Germany

Bone is a complex composite material with similarities to hierarchically structured functional materials. In the case of a fracture or the need for a replacement (e.g. hip prosthesis) filler or replacement materials are necessary. Next generation bone implants are functionalised with drugs to stimulate bone healing locally or to provoke antibiotic effects. Here we focus on the release and dispersion of the anti-osteoporotic agent Sr^{2+} from strontium enriched bone cement. The knowledge of the release and dispersion kinetics of the drug plays an eminent role for the performance optimisation of the biomaterial.

Due to practical and technical reasons it is almost impossible to track the drug release kinetics, drug dispersion and the degradation of the implant material in vivo. Here we apply time of flight secondary ion mass spectrometry (ToF-SIMS) depth profiling to obtain the diffusion coefficient of Sr^{2+} in the mineralised areas of healthy and osteoporotic rat bone in post mortem examinations. For data evaluation of the depth profiles in mineralised bone we applied a simple diffusion model. The obtained diffusion coefficient for trabecular osteoporotic bone is with 1.76×10^{-10} cm^2/s more than two decades higher than that for healthy bone (2.91×10^{-12} cm^2/s). In cortical bone no significant difference in the diffusion coefficient (healthy 1.33×10^{-12} cm^2/s, osteoporotic 4.17×10^{-12} cm^2/s) could be found. The varying diffusion coefficients can be explained by the different bone nanostructure, which was investigated by focused ion beam scanning electron microscopy (FIB-SEM) and high-resolution transmission electron microscopy (HR-TEM).

The data of cement dissolution experiments into water in combination with inductively coupled plasma mass spectrometry (ICP-MS) analysis account for dissolution kinetics following Noyes-Whitney rule. For dissolution in A-MEM cell culture media the process is kinetically hindered and can be described by Korsmeyer-Peppas kinetics. An adsorbed protein layer on top of the cement surface, which was detected by ToF-SIMS, is responsible for the kinetic inhibition. Based on the results of various analytical experiments we developed a two-phase model and performed a finite element calculation for the release and dispersion of Sr^{2+} in bone. The validity of the applied model is proven by animal experiments. We compared the calculated images to mass spectrometric images of bone cross sections and achieved good conformity. It appears that drug removal via the vascular system is negligible. This is a good basis for predictions of drug mobility in bone.

10:20am **BI+AS+NS-FrM7 Spatial Distributions of Epithelial Growth Factors in Hydrogels Studied by ToF-SIMS and TIRF Microscopy for the Development of Biocompatible Multiple-protein Delivery Systems for Wound Healing***, **Shohini Sen-Britain,*** State University of New York, Buffalo*; W. Hicks,* Roswell Park Comprehensive Cancer Center*; J.A. Gardella Jr.,* State University of New York, Buffalo

This work reports the use of ToF-SIMS imaging, TIRF microscopy, and depth profiling to visualize and map the interactions of (hydroxyethyl)methacrylate (HEMA)-based hydrogels with mixtures of growth factors that are often secreted by the epithelium during wound healing. During re-epithelialization, hydrogels can act as both tissue scaffolds at the interface between healing epithelium and surrounding connective tissue, and as delivery vehicles of therapeutic proteins that expedite the wound healing process.

The spatial distribution of multiple growth factors at hydrogel surfaces can influence biocompatibility and release kinetics, orientation and conformation of the individual growth factors. Hydrogels interact with mixtures of growth factors in vivo and also when they are developed into multiple-protein delivery systems. To address these concerns, this work presents 2D and 3D spatial distributions of fluorophore-labeled growth factors varying in size, secondary structure, and hydrophobicity at the hydrogel surfaces to model the interface between porous, phase segregated drug delivery systems and complex macromolecular mixtures.

HEMA hydrogel blends incorporating methyl methacrylate (HEMA/MMA) and methacrylic acid (HEMA/MAA) cause increased hydrophobicity or hydrophilicity at the hydrogel surface, respectively. They also present phase segregation and porous topography at the surface. Depth profiling shows that smaller proteins, such as epidermal growth factor (EGF) permeate deeper into porous regions than larger proteins such as keratinocyte growth factor (KGF) and platelet-derived growth factor (PDGF). SIMS and TIRF imaging shows that proteins with more hydrophobic character such as PDGF and EGF localize at phase segregated regions containing MMA, while those with more hydrophilic character such as KGF localize at phase segregated regions containing MAA or HEMA. Biological ramifications of these results regarding biocompatibility and multiple-protein delivery systems are the focus of future work.

Nanometer-scale Science and Technology Division
Room 102B - Session NS+AM+AS+MN+PC+PS+SS+TR-FrM

SPM – Probing Chemical Reactions at the Nanoscale

Moderators: Phillip First, Georgia Institute of Technology, An-Ping Li, Oak Ridge National Laboratory

8:20am **NS+AM+AS+MN+PC+PS+SS+TR-FrM1 Using Self-Assembly to Engineer Electronic Properties in 1D and 2D Molecular Nanostructures***, **Michael F. Crommie,*** University of California at Berkeley Physics Dept. **INVITED**

Control of chemical reactions at surfaces has created new opportunities for on-surface synthesis of low-dimensional molecular nanostructures. By designing precursor molecules it is possible to engineer new bottom-up structures with atomic precision and predetermined electronic properties. We have used this technique to confirm recent predictions that quasi-1D graphene nanoribbons (GNRs) have well-defined electronic topology. This means that when “topologically non-trivial” GNRs are fused to “topologically trivial” GNRs then a singly-occupied, topologically-protected interface state occurs at the boundary between them. This has allowed us to engineer new GNRs with unique electronic structure. We have also engineered molecular precursors to control the behavior of 2D polymers. By tuning the coupling reaction between monomers it is possible to create 2D covalent organic frameworks (COFs) that exhibit novel electronic superlattice behavior.

9:00am **NS+AM+AS+MN+PC+PS+SS+TR-FrM3 Chemical and Electronic Structure of Aniline Films on Silica Surfaces***, **Christopher Goodwin,*** University of Delaware*; A.J. Maynes,* Virginia Polytechnic Institute and State University*; Z.E. Voras,* University of Delaware*; S.A. Tenney,* Center for Functional Nanomaterials Brookhaven National Laboratory*; T.P. Beebe,* University of Delaware

The use of silica as a substrate for polyaniline is highly appealing since silica is a common component in photovoltaics. To this end we have developed a vacuum technique for the deposition and functionalization of silica with aniline, without the need for wet chemistry. To study the chemistry of the reaction, X-ray Photoelectron Spectroscopy (XPS), Time-of-Flight Secondary Ion Mass Spectroscopy (TOF-SIMS), and Atomic Force Microscopy (AFM), among other techniques, have been used. To determine the electronic structure if the resulting films, scanning tunneling microscopy and evaluation of valance band data collected by XPS was performed. By controlling the temperature of the gas-phase reaction, two states of aniline were found to exist on the silica surface. Our interest is in determining how the two states affect the electronic band structure of the surface.

9:20am **NS+AM+AS+MN+PC+PS+SS+TR-FrM4 Electric Field Driven Chemical Reaction of Individual Molecular Subunits by Scanning Tunneling Microscopy***, **Tomasz Michnowicz,*** Max Planck Institute for Solid State Research, Germany, Deutschland*; B. Borca,* Max Planck Institute for Solid State Research, Germany*; R. Pétuya,* Donostia International Physics Centre, Spain*; M. Pristl, R. Gutzler, V. Schendel, I. Pentegov, U. Kraft, H. Klauk,* Max Planck Institute for Solid State Research, Germany*; P. Wahl,* University of St Andrews, UK*; A. Arnau,* Donostia International Physics Centre, Spain*; U. Schlickum, K. Kern,* Max Planck Institute for Solid State Research, Germany

Understanding of elementary steps and control in chemical reactions on the atomic scale might improve significantly their efficiency and applicability. Scanning tunneling microscopy (STM) allows both investigating and stimulating chemical reactions of individual organic subunits, for example via the tunneling current, electric field or a mechanical interaction. Here we present a study of an STM stimulated desulfurization process of the thiophene functional group embedded in a tetracenothiophene (TCT) molecule on a Cu(111) surface. Precise positioning and applying stimuli with the STM tip apex allows determination of a two-step process responsible for this chemical reaction. High resolution STM images, supported by the DFT calculations, help us to correlate the first reaction step to the breaking of one the carbon-sulfur bonds and the second to the breaking of the second carbon-sulfur bond. The latter reaction also results in a significant increase of the bond strength of the broken thiophene part to Cu surface atoms. The chemical reaction is triggered by positioning the tip apex above the thiophene part and applying a threshold voltage that depends linearly on the tip-molecule distance. This linear dependence is a hallmark of an electric field driven process. In addition, conduction measurements through single TCT molecules before and after the reaction have been performed. Compared to the intact molecule we observed a 50% increase of conductance after the chemical reaction, which is in agreement with the finding of a much stronger bond formation between the molecule and Cu surface atoms.

9:40am **NS+AM+AS+MN+PC+PS+SS+TR-FrM5 Characterising Conjugated Polymers for Organic Electronics by High-resolution Scanning Probe Microscopy***, **Giovanni Costantini,*** University of Warwick, UK

The structure of a conjugated polymer and its solid-state assembly are without a doubt the most important parameters determining its properties and performance in (opto)-electronic devices. A huge amount of research has been dedicated to tuning and understanding these parameters and their implications in the basic photophysics and charge transporting behaviour. The lack of reliable high-resolution analytical techniques constitutes however a major limitation, as it hampers a better understanding of both the polymerisation process and the formation of the functional thin films used in devices.

Here, by combining vacuum electrospray deposition and high-resolution scanning tunnelling microscopy (STM) we demonstrate the ability of imaging conjugated polymers with unprecedented detail, thereby unravelling structural and self-assembly characteristics that have so far been impossible to determine.

Applying this novel technique to prototypical DPP- and thiophenes-containing polymers, we show that sub-molecular resolution STM images allow us to precisely identify the monomer units and the solubilising alkyl side-chains in individual polymer strands. Based on this, it becomes possible to determine the molecular number distribution of the polymer by simply counting the repeat units. More importantly, we demonstrate that we can precisely determine the nature, locate the position, and ascertain the number of defects in the polymer backbone. This unique insight into the structure of conjugated polymers is not attainable by any other existing analytical technique and represents a fundamental contribution to the long-discussed issue of defects as a possible source of trap sites. Furthermore, the analysis of our high-resolution images, also reveals that the frequently assumed all-trans-conformation of the monomers in the polymer backbone is actually not observed, while demonstrating that the main driver for backbone conformation and hence polymer microstructure is the maximization of alkyl side-chain interdigitation.

10:00am **NS+AM+AS+MN+PC+PS+SS+TR-FrM6 Probing Electrical Degradation of Lithium Ion Battery Electrodes with Nanoscale Resolution***, **Seong Heon Kim**,* Samsung Advanced Institute of Technology, Republic of Korea*; S.Y. Park, H. Jung,* Samsung Advanced Institue of Technology, Republic of Korea

The high performance of lithium-ion batteries (LIBs) is in increasing demand for a variety of applications in rapidly growing energy-related fields, including electric vehicles. To develop high-performance LIBs, it is necessary to thoroughly understand the degradation mechanism of LIB electrodes. The investigation of the electrical conductivity evolution during cycling can lead to a better understanding of the degradation mechanism in cathode and anode materials for Li-ion batteries. Here, we probed the electrical degradation of LIB electrodes with nanoscale resolution via quantitative and comparative scanning spreading resistance microscopy (SSRM). First, the electrical degradation of $\mathrm{LiNi_{0.8}Co_{0.15}Al_{0.05}O_2}$ (NCA) particles which are representative LIB cathode materials was studied [1]. After 300 charge/discharge cycles, stepwise-increasing resistance distributions toward the centers of the secondary particles were observed. These distributions correspond to the degenerated granular structures of the secondary particles caused by the formation of micro-cracks. Second, the electrical degradation of LIB anodes, the blended Si-C composites with graphite (Gr) particles, was investigated using SSRM [2]. From the SSRM measurements, it was obviously demonstrated that the electrical conductivity of the Si-C composite particles is considerably degraded by 300 cycles of charging and discharging, although the Gr particles maintain their conductivity. Our approach using SSRM techniques can be a good tool to study the electrical properties of various LIB electrode materials with nanoscale resolution.

[1] S.Y. Park, W.J. Baek, S.Y. Lee, J.A. Seo, Y.-S. Kang, M. Koh, S.H. Kim, Probing electrical degradation of cathode materials for lithium-ion batteries with nanoscale resolution, Nano Energy 49 (2018) 1–6.

[2] S.H. Kim, Y.S. Kim, W.J. Baek, S. Heo, D.-J. Yun, S. Han, H. Jung, Nanoscale electrical degradation of silicon-carbon composite anode materials for lithium-ion batteries, Submitted.

Surface Science Division
Room 203C - Session SS+AS+HC-FrM
Near/Ambient Pressure and Bridging Gaps between Surface Science and Catalysis

Moderators: Donna Chen, University of South Carolina, Janice Reutt-Robey, University of Maryland College Park

8:20am **SS+AS+HC-FrM1 Ambient Pressure Electron Spectroscopy (XPS, XAS) and Electron Microscopy Studies of the Structure and Chemistry of Nanostructured Model Catalysts***, **John Hemminger**,* University of California Irvine **INVITED**

We use physical vapor deposition to create a high density of metal oxide nanoparticles on highly oriented pyrolytic graphite (HOPG). Photoelectrochemical methods are then utilized to selectively decorate the metal oxide nanoparticles with transition metal nanoparticles. This talk willl describe our studies of the Pt/$\mathrm{TiO_2}$/HOPG ; Cu/ZnO/HOPG systems. The nanostructured surfaces are characterized by SEM, TEM, XPS, and synchrotron based XAS. Lab-based and synchrotron based ambient pressure XPS experiments have been used to study the CO oxidation reaction on Pt/$\mathrm{TiO_2}$/HOPG and the $\mathrm{CO_2}$ reduction reaction on $\mathrm{CuO_x}$/$\mathrm{TiO_2}$/HOPG. In addition, the catalytic activity of $\mathrm{CuO_x}$/$\mathrm{TiO_2}$/HOPG for electrochemical $\mathrm{CO_2}$ reduction has been studied using differential electrochemical mass spectrometry (DEMS).

9:00am **SS+AS+HC-FrM3 *In-operando* Investigation of the Initial Oxidation Stages for NiCr-(W) Alloys with X-ray Photoelectron Spectroscopy***, **Cameron Volders**, V. Angelici Avincola, P. Reinke,* University of Virginia

Ni-Cr alloys are of technical interest as they exhibit superior corrosion resistance due to the formation of a passive chromia film which helps protect the underlying alloy from degradation, and limits catastrophic events such as pitting and crevice corrosion. A wide range of Ni-Cr alloys have been developed to satisfy industrial needs and the properties for each alloy differ slightly based on its application. The properties are controlled by manipulating Cr content as well as adding minor alloying elements such as Mo or W, which have been shown to enhance corrosion resistance. The ideal composition for these alloys has been optimized over many decades but the mechanistic understanding of the role of Mo or W additions is not fully developed.

The current work presents an *in-operando* ambient pressure – X-ray photoelectron spectroscopy (AP-XPS) study which investigated the early stages of oxidation for four alloy concentrations; (1) Ni-5% Cr, (2) Ni-15% Cr, (3) Ni-30% Cr, and (4) Ni-15% Cr-6% W by weight percent between 573 and 773 K and $p(\mathrm{O_2}) < 0.1$mbar. The primary objectives were to elucidate how varying Cr content in the alloys and the addition of W impacts the nucleation and growth of different oxide phases. The modulation of alloy and oxide composition and bonding was observed over an extended time period delivering a detailed view of the reaction pathways.

A key result from this work is the Cr surface segregation in the alloys prior to oxidation, which contributes to the rapid nucleation of Cr-oxides in the first reaction step with $\mathrm{O_2}$. The surface enrichment of Cr influences the initial nucleation of the different oxide species and prejudices the progression of oxide growth. The main portion of this work will focus on the time evolution of the different oxide phases and the kinetics of Ni-oxide and Cr-oxide formation for all alloys, which allows to build a detailed model of the reaction. An additional component accounts for a substantial portion of the oxide signal, and is interpreted as the combination of spinel and non-stoichiometric oxide. The addition of W in the alloy resulted in a near complete suppression in the formation of Ni oxide species, and different models to interpret the impact of W on the progression of the oxidation reaction will be discussed.

9:20am **SS+AS+HC-FrM4 Surface Hydroxylation of Polar (000-1) and Non-polar (11-20) ZnO Probed with AP-XPS***, **Sana Rani**, A. Broderick, J.T. Newberg,* University of Delaware

The interaction of ZnO with water vapor has been an important topic of research due to the relevance for numerous catalytic processes including water-gas shift reaction, methanol synthesis, olefin hydrogenation, and gas sensor applications. ZnO based humidity nanosensors were found to have high sensitivity towards humidity and fast response time in heterogeneous catalysis. The presence of water strongly modifies the surface properties depending on the substrate and coverage. The adsorbed water can catalyze heterogeneous reactions and corrosion by proton transfer and solvating products. Dissociation of adsorbed water is of particular interest for catalysis, as this may be the first step in the activation of water molecules for chemical reactions. In this work, surface thermodynamic calculations were applied to synchrotron based ambient pressure X-ray photoelectron spectroscopy (AP-XPS) data to investigate the interface between water vapor and the low index polar (000-1) and non-polar (11-20) ZnO surfaces. Three isobaric experiments were performed over a range of temperatures from 10 to 500°C. It is hypothesized that observed hydroxyl groups, adsorbed water and carbonates on the ZnO surface can significantly influence heterogeneous catalytic reactions under ambient conditions.

9:40am **SS+AS+HC-FrM5 Reason of High Stability and Reactivity of Ni/silicalite-1 Catalyst for Dry Reforming of Methane***, **Evgeny Vovk**, X. Zhou, Z. Liu, C. Guan, Y. Yang,* ShanghaiTech University, China*; W. Kong,* Shanghai Advanced Research Institute, China*; R. Si,* Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chaina

Dry reforming of methane (DRM) is an environmentally favored process transferring two greenhouse gases ($\mathrm{CH_4}$ and $\mathrm{CO_2}$) into syn-gas ($\mathrm{H_2}$+CO). Ni-based catalysts demonstrate good potential in this application because of comparable reactivity and low cost. DRM is highly endothermic reaction which requires high operating temperatures. At high temperatures sintering is a common issue of catalyst deactivation. Deactivation of Ni catalyst in DRM process is also accompanied by carbon deposition (coking) induced by methane decomposition and CO disproportionation (Boudouard reaction).

In the current work we investigated catalyst obtained by encapsulating Ni clusters (2.5±0.2 nm) into microporous silicalite-1 (aluminum free zeolite with MFI structure). No deactivation and coking under a wide range of conditions where carbon formation is thermodynamically favorable were observed for this sample. This atom-economical Ni/silicalite-1 catalyst was compared with Ni/$\mathrm{SiO_2}$ catalyst prepared by impregnation method. XPS study has been performed in ThermoFischer ESCALAB 250X photoelectron spectrometer. The gas treatments of catalysts (up to 1 bar) was performed in high pressure gas cell (Model HPGC 300, Fermi Instruments) connected to the spectrometer.

XPS analysis of Ni/silicalite-1 demonstrates the presence of a peak with binding energy (BE) 856.2 eV in Ni $2p_{3/2}$ region. Nickel silicate has a similar spectrum shape with close BE. The presence of this peak in Ni/silicalite-1 sample suggests of the Ni-O-Si species and strong metal-support interaction. After oxidation of this sample at 400°C there are no changes of the Ni-O-Si species. At the same time nickel in Ni/$\mathrm{SiO_2}$ catalyst which has shown mostly metallic Ni^0 state with minor content of Ni-O-Si upon oxidation transforms into NiO. Reduction of Ni/silicalite-1 catalyst in hydrogen at 650°C leads to partial reduction of nickel into Ni^0 while a significant portion of Ni-O-Si still remains. The behavior of Ni-O-Si feature in both oxidizing and reducing conditions clearly indicates its very high stability. We attribute this feature to the Ni-O-Si formed at the interface between Ni nanoparticles and the silicalite support. The Ni/silicalite-1 novel oxygen-philic interfacial catalyst system consists of very small metallic Ni clusters intercalated into silicalite framework and surrounded by Ni-O-Si species. Ni-O-Si provides high stability of Ni nanoparticles and prevents sintering and carbon deposition making this catalyst also very interesting for commercial application.

10:00am **SS+AS+HC-FrM6 Recent Development in XPS and Ambient Pressure XPS Techniques***, **Lukasz Walczak**,* PREVAC sp. z o.o., Poland

Many important processes such as energy conversion, electrochemical, corrosion and biological processes take place at solid-gas and solid-liquid interfaces [1-3]. X-ray photoelectron spectroscopy (XPS) is the most powerful technique for understanding of these processes at the atomic level and it is the key to improving the performance of novel battery generation or renewable energy sources such as solar, wind or hydropower energy conversion devices. We would like to promote the latest equipment, technology solutions and innovations for the photoelectron spectroscopies field. Here it will be presented an innovative and compact spectrometers for the routine X-ray photoemission spectroscopy and ambient pressurephotoemission spectroscopy for study of important phenomena in the current research. The design, construction, and technical parameters of new analyser will be presented. We will report the research results of XPS measurements conducted on the photovoltaic [4], catalytical [5] or bio-materials. Moreover, it will be demonstrated the analyser operation in ambient pressure. Also the results of interaction of oxygen and surface alloy will be presented, in order to permit complete characterization for the different pressure and temperature conditions.

References

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10:20am **SS+AS+HC-FrM7 Quantum Mechanics and Reaction Kinetics Study on SiO_2 and SiN Dry Isotropic Chemical Etching Process***, **Taiki Kato**, M. Matsukuma, K. Matsuzaki, L. Chen,* Tokyo Electron Technology Solutions Limited, Japan

Dry isotropic chemical etching processes are important for semiconductor manufacturing, but such processes often require subtle process tuning to achieve high etching rates and the desired etching selectivity between SiO_2 and SiN. For example, the dry chemical etching solely with HF gas (Process 1) requires fine tuning of conditions for SiN etching rate because it has a peaky dependence on the process temperature; whereas dry chemical etching with NH_3/HF binary gas mixtures (Process 2) requires subtle tuning to simultaneously maximize etching rate and SiO_2:SiN selectivity. Notably, in Process 2, SiN etching rate increases with the etching time while SiO_2 etching rate slows down with the etching time. This slowdown is attributed to the formation of an etchant diffusion barrier from the solid byproduct, AFS (Ammonium fluorosilicate). Because of these contradictions, it has been difficult to achieve highly selective and rapid SiO_2 etching, thus a better understanding of the etching mechanisms is important to further develop the high selectivity required for the formation of scaled multicomponent semiconductor device structures. This study therefore focuses on revealing these mechanisms by using the quantum mechanics and by the analysis of reaction kinetics.

Firstly, Process 1 was studied with a quantum mechanical analysis by using the GRRM (Global Reaction Route Mapping) program. For this study, GRRM searched possible etching reaction paths automatically. From this reaction path search, it was revealed that SiN etching by HF gas, when used by itself, is much more rapid than SiO_2 etching. Further analysis was conducted by the reaction kinetics analysis. The kinetics parameters comprised HF adsorption, desorption and etching reactions. This model shows good agreement with the experimental SiN etching behavior.

Moreover, Process 2 was studied with similar quantum mechanics and kinetics analyses. Quantum mechanics analysis revealed that NH_3 combined with HF enhances both SiO_2 and SiN etching reactions. An NH_4F etching model was then added to the kinetics model. Because the etching byproduct, AFS, may be both an SiN etching accelerator and an SiO_2 etching decelerator, we could model the SiN etching kinetics initiated by NH_4F and propagated by NH_4F + AFS. This model quantitatively agrees with the experimental SiN etching data. Likewise, the SiO_2 kinetics model is composed of NH_4F etching, the diffusion resistance through solid AFS and the sublimation of AFS. This model also shows good agreement with experiment.

These analyses reveal the chemical etching mechanisms and enable process optimization. Further discussion will be presented on AVS 65th.

10:40am **SS+AS+HC-FrM8 Viscosity and Surface Tension Effects on Metal Sputtered onto Low Vapor Pressure Liquids***, **Mark De Luna**, M. Gupta,* University of Southern California

Sputtering onto low vapor pressure liquids has garnered a lot of attention due to the ease of creating metal thin films and nanoparticles. However, the effects of the liquid viscosity and surface tension on the resulting morphologies has been neglected. In this work, we studied DC magnetron sputtering of gold and silver onto liquid substrates of varying viscosities and surface tensions. We were able to decouple the effects of viscosity from surface tension by depositing the metals onto silicone oils with a range of viscosities. The effects of surface tension were studied by depositing the metals onto squalene, poly(ethylene glycol), and glycerol. It was found that dispersed nanoparticles formed on liquids with low surface tension and low viscosity whereas dense films formed on liquids with low surface tension and high viscosity. We also observed that nanoparticles formed on both the liquid surface and within the bulk liquid for high surface tension liquids. Our results can be used to tailor the metal and liquid interaction to facilitate the fabrication particles and films for various applications.

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