Applied Surface Science Division
Room A211 - Session AS+BI+RA-MoM

Quantitative Surface Analysis I/Reproducibility Issues in Quantitative XPS

Moderators: Donald Baer, Pacific Northwest National Laboratory, Mark Engelhard, EMSL, Environmental Molecular Sciences Laboratory

8:20am **AS+BI+RA-MoM-1 Improving Accuracy in Quantitation by XPS: Standards, Cross-sections, Satellite Structure***, **C. Richard Brundle**,* C.R.Brundle & Associates*; P Bagus,* University of North Texas*; B Crist,* XPS International LLC **INVITED**

Determining elemental composition by XPS requires determining relative peak intensities from the elements concerned, and then normalizing using Relative Sensitivity Factors (RSF's). Such RSF's are usually generated from standard materials using the intensity from the "main" peak only and ignoring any associated satellite structure (shake-up, shake-off, and multiplet splitting components) intensity. In the seminal paper by Wagner, et al, (1) this resulted in a conclusion that the calculated Li(1s) photoionization cross-section, σ, (2) was too low by ~40%, relative to F(1s). This apparent discrepancy cast doubt on the claimed 5% accuracy of the calculated σ values for low Z elements (2). We show that this is incorrect. The discrepancy is due, primarily, to the fact that Li(1s) loses almost zero intensity from the main peak into associated satellites, whereas for F1s it is substantial, *spreading over 100ev to lower KE*. A calculated σ always refers to the *total* intensity of photoemission from the orbital concerned, including any intrinsic satellite structure. In addition, the experimental Li(1s) peak intensity in Wagner, et al. (1) was actually *overestimated*, owing to inclusion of overlapping satellite structure spreading from the nearby F(2s) peak. For the 1s intensities of the first row elements, a crude theoretical approximation predicts the total intensity lost from the "main" peak to satellites quite well. It involves an exponential dependence on the number of valence shell electrons present, which for Li+ of LiF, is zero, and for F- is 6 (the filled 2p shell), yielding values of zero loss for Li+ and 20-30% for F-. Full a*b initio* quantum calculations for these ions support the crude estimate (calculated Li+ losses are 1.4%; F- losses are 22.7%). In contrast to earlier claims to the contrary(3), satellite losses, for elements across the periodic table, vary widely from core-level to core level, element to element, *and most critically with the bonding situation of an element (see, for example ref 4*). Thus any "universal" element RSF's, using main peak intensities only, though semi-quantitatively useful, are inherently limited in potential accuracy achievable, sometimes by up to a factor of 2. What is needed, for improved accuracy, are sets of RSF's appropriate to different bonding situations. Such sets would be particularly useful for the current large inexperienced XPS user base. We attempt to give guidelines.

C.D. Wagner, et al, Surf. Interface Anal. **3**, 211, 1981

J.H. Scofield, J. Elec. Spec. **8**, 129, 1976

V.G. Yarzhemsky, et al, J. Elec. Spec. **123**, 1, 2001

P. S. Bagus, E. Ilton, and C. J. Nelin, Catalysis Letters, **148**, 1785, 2018

9:00am **AS+BI+RA-MoM-3 A Rigorous Approach to the Calculation of the Uncertainties in XPS Analysis***, A Herrera-Gomez,* CINVESTAV-Unidad Queretaro, México*; **Orlando Cortazar-Martinez**,* CINVESTAV-Unidad Queretaro, Mexico

One of the most important applications of X-ray photoelectron spectroscopy (XPS) is the characterization of the chemical composition of solids near the surface. However, the proper assessment of the associated uncertainties has remained an elusive problem. One of the issues is that the total uncertainty comes from various sources: the experimental data (peak intensities), parameters theoretically calculated (cross-section, mean-free-path), and parameters associated to the XPS equipment (angular and kinetic energy transmission functions).

The uncertainty on most of these parameters should be treated as systematic errors. The most important non-systematic uncertainty comes from the peak intensities [1]. It is a common practice in XPS data peak fitting to first subtract the background and then peak-fit the backgroundless data (*static* approach [2]). This approach prevents the use of the covariance matrix to calculate uncertainties because the covariance with the parameters defining the background cannot be accounted. It is only under the *active* approach [2] that it is possible to account for the covariance with the background parameters because the background is optimized in conjunction with the peak parameters. In this paper, the assessment of the uncertainty on the peak intensities will be treated in detail, as well as the total uncertainty on the composition.

[1] A. Herrera-Gomez, A rigorous approach to the calculation of the uncertainties in XPS analysis (Internal Report), Internal Report, Internal Report. CINVESTAV-Unidad Queretaro, n.d. http://www.qro.cinvestav.mx/~aherrera/reportesInternos/uncertaintiesXPS.pdf.

[2] A. Herrera-Gomez, M. Bravo-Sanchez, O. Ceballos-Sanchez, M.O.O. Vazquez-Lepe, Practical methods for background subtraction in photoemission spectra, Surf. Interface Anal. 46 (2014) 897–905. doi:10.1002/sia.5453.

9:20am **AS+BI+RA-MoM-4 Gross Errors in XPS Peak Fitting***, **Matthew Linford**, V Jain, G Major,* Brigham Young University

X-ray photoelectron spectroscopy (XPS) is the most important method for chemically analyzing surfaces. It is widely used in numerous areas of research and technology. Many research groups and individuals are skilled at analyzing XPS data. However, too much of what has appeared and continues to appear in the literature is of at best questionable value and accuracy. In this talk, I will discuss some of the all too common gross errors. Both correct and incorrect examples of each of the following will be shown. (i) Not plotting the data according to international convention of binding energy increasing to the left. (ii) Fitting and interpreting data that are far too noisy to be interpreted. (iii) Labeling noise as chemical components. (iv) Not showing the original data – only showing the synthetic (fit) peaks and their sum. (v) Not plotting the sum of the fit components with the original data. (vi) Having widely varying peak widths in a fit. (vii) Having the baseline completely miss the noise on either side of the peak. (viii) Not collecting data over a wide enough energy window to see a reasonable amount of baseline on both sides of the peak envelope. (ix) In a C 1s spectrum, reversing the labeling on the C-O and C=O peaks, and other mislabeling issues. The C 1s peak envelope is well understood so there shouldn't be huge mistakes here. (x) Not taking into account spin-orbit splitting when it is necessary. (xi) In a comparison of spectra, having widely differing peaks and peak positions for components that are supposed to be the same between the spectra.

9:40am **AS+BI+RA-MoM-5 Improved Energy Referencing in XPS***, **Hagai Cohen**,* Weizmann Institute of Science, Israel

Basically, energy referencing in XPS relies on an absolute reference provided at the back contact of the sample: the electrical ground. If poor connectivity is encountered between the studied surface and ground, reference signals may be used to derive correction terms for the energy scale, such as to get the proper binding energies for elements of interest. Unfortunately, in many cases this procedure fails to accurately address differential charging effects, namely local and temporal variations in the surface charge and the related electrostatic potential.

In the present work, a method for introducing a second absolute/external reference is described. The technical improvement is proven to be mandatory. It enables advanced analyses of binding energies, which refines the chemical analysis significantly. The method further reveals intriguing cases in which the x-ray induced charging does not follow the trivially expected behavior. On top of that, an access to rich electrical information is realized as soon as a second reference is introduced, thus expanding the XPS capabilities into new areas. Measurements of the inherent inner fields in semiconductors and the reliable derivation of device band diagrams, free of the beam-induced artifacts, are just a few examples to be mentioned.

10:00am **AS+BI+RA-MoM-6 How to Avoid Errors in the Interpretation of XPS Data?***, **Andreas Thissen**, P Dietrich,* SPECS Surface Nano Analysis GmbH, Germany*; W Unger,* Bundesanstalt für Materialforschung und -prüfung - Berlin (Germany), Germany

Over the last fifty years significant developments have been done in photoelectron spectroscopy instrumentation and thus opened new fields of application. Especially XPS or ESCA developed into a standard analytical method in many labs for surface and material characterization. The number of users and the number of publications using XPS data has tremendously increased. But as a side effect it is a challenge to keep the level of knowledge about the method and correct data interpretation at a high level for all users of these data.

To avoid errors in the interpretation of XPS data instrument manufacturers put efforts inside their instruments and software packages to help and guide the user through data acquisition, data quantification and interpretation and finally also through data reporting. By this data can be made compatible with existing ISO and other community standards. But even more, data quality becomes transparent also in times of open source publications and open data repositories.

This paper summarizes the challenges of data handling, data treatment, data storage, parameter-data correlation, expert systems for data acquisition, reporting assistance and tracking and authorization tools for sensitive data. In summary future perspectives and suggestions are discusses for improved data repeatability and data reliability.

10:40am **AS+BI+RA-MoM-8 Misinterpretations in the Spectroscopic Analysis of Heterogeneous Materials and Defected Structures***, **Lisa Swartz**, K Artyushkova, J Mann, B Schmidt, J Newman,* Physical Electronics

Analysis of samples where lateral heterogeneities can be present at a variety of scales poses a challenging spectroscopic task. In routine applications of XPS spectroscopy, the analyst is usually acquiring spectra over a large area from multiple positions on the sample and derives conclusions on "representative" chemical composition from average atomic concentrations and standard deviations. However, if lateral heterogeneities existing at the surface have smaller physical dimensions as the analysis area, the conclusions on "representative" chemical composition derived from large area spectroscopy will be erroneous. For accurate structural analysis of heterogeneous materials, it is very important to understand the scale of heterogeneity beforehand, so that the analysis areas and the size of the X-ray probe used for analysis are chosen appropriately. Often, complimentary microscopic techniques, such as SEM, are performed before XPS analysis which addresses some of this challenge but does not allow analysis over the same area.

The ability to perform small area spectroscopy for studying the heterogeneity and physical dimensions of samples is critical for obtaining accurate information on sample structure. In this talk, we will show examples of inaccurate use of large area spectroscopy and discuss the experimental approach towards selecting the relationship between the X-ray size and physical scale of defects and heterogeneities at the surface required to obtain an accurate representation of heterogeneous sample structure.

11:00am **AS+BI+RA-MoM-9 Current Issues and Solutions for Reliable, Robust and Reproducible XPS Spectral Acquisition and Data Reporting***, J Counsell, C Blomfield,* Kratos Analytical Limited, UK*; **Christopher Moffitt**,* Kratos Analytical Limited*; N Gerrard, S Coultas,* Kratos Analytical Limited, UK

XPS is now a truly interdisciplinary technique used in a wide variety of fields including catalysis, tribology, bioremediation and nuclear energy. With more than 1000 instruments currently in use, the ubiquitous nature of XPS means there is a greater requirement than ever for clarity regarding spectral acquisition, analysis and interpretation. The XPS user base has changed significantly – no longer the field of dedicated "technical experts" and spectroscopists – requiring instruments to be simple to use with a higher degree of automation in all parts of operation and analysis.

Here we will discuss the overall procedure for the technique specifying the critical steps in generating sound data and conclusions. Pitfalls and perils in the following steps will be briefly discussed: surface charging, beam damage, contamination, peak identification, energy calibration, quantification, peak-fitting, database usage, chemical state assignment and error reporting as will the latest methods implemented in mitigating against these issues. Worked examples and user studies will be presented to illustrate common inconsistencies.

11:20am **AS+BI+RA-MoM-10 Intensity Calibration and Sensitivity Factors for XPS Instruments with Monochromatic Ag Lα and Al Kα Sources***, **Alexander Shard**,* National Physical Laboratory, UK*; J Counsell, C Blomfield,* Kratos Analytical Limited, UK*; D Cant,* National Physical Laboratory, UK*; E Smith,* University of Nottingham, UK*; P Navabpour,* Teer Coatings Ltd, UK

The use of monochromated Ag La X-ray has been described previously.[1, 2] These sources have now become more widely available on commercial instruments and easier to use due to automation and the superior collection efficiency of modern analysers. To enable direct comparison between data acquired using both sources it is essential to be able have a common calibration scheme and a set of useful sensitivity factors. We employ the calibration method developed by the National Physical Laboratory for Al Kα sources[3] and extend this for Ag Lα sources.[4] Sensitivity factors for Ag Lα and Al Kα are calculated from photoionisation cross sections and electron effective attenuation lengths. These compare well to previous experimental values and data acquired from ionic liquids. The intensity of the Ag Lα source is found to be approximately 50 times lower than the Al Kα source. This, coupled with generally lower photoemission efficiencies, results in noisier data or extended acquisition times. However, there are clear advantages to using the Ag Lα source to analyse certain elements where additional core levels can be accessed and for many technologically important elements where interference from Auger electron peaks can be eliminated. The combination of calibrated data from both sources provides direct and easily interpreted insight into the depth distribution of chemical species. This could be particularly important for topographic samples, where angle resolved experiments are not always helpful. We also demonstrate, using thin coatings of chromium and carbon, that the inelastic background in Ag Lα wide-scan spectra has a significantly increased information depth compared to Al Kα.

References

1. Yates, K.; West, R. *Surf. Interface Anal.* **1983,***5* (4), 133-138.

2. Edgell, M.; Paynter, R.; Castle. *J. Electron Spectr. Rel. Phenom.* **1985,***37* (2), 241-256

3. Seah, M. P.. *J. Electron Spectr. Rel. Phenom.* **1995,***71* (3), 191-204.

4. Shard, A. G. *et al*. *Surf. Interface Anal.* **2019**https://doi.org/10.1002/sia.6647

11:40am **AS+BI+RA-MoM-11 Reporting XPS Measurements and How Can We Do Better to Minimize Reproducibility Problems***, **Karen Gaskell**,* University of Maryland, College Park

The level of detail and information provided in the average scientific article reporting XPS measurement and analysis varies widely. In some cases journal page limitations limit the inclusion of information such as experimental details, instrumental parameters and data sets that are required to fully describe the data collection and subsequent analysis so that it can be adequately reproduced by others. In other cases important information is simply left out. What are the minimum and preferable types of information we should include when reporting XPS results?

Biomaterial Interfaces Division
Room A120-121 - Session BI+AS+NS-MoM

Biofabrication, Bioanalytics, Biosensors, Diagnostics, Biolubrication and Wear

Moderators: Joe Baio, Oregon State University, Caitlin Howell, University of Maine

8:20am **BI+AS+NS-MoM-1 Bio-inspired Peptide-polymer Hybrid Mucin Analogues: Applications in Osteoarthritis and Kidney Stone Disease***, **Daniel L. French**, L Navarro, S Zauscher,* Duke University

Mucins play diverse and crucial roles in the body. These functions range from lubrication of articular joints and the eye, to protection of stomach endothelium, to modulation of oral and gut microflora populations. Despite their diversity, these functions commonly stem from modifications in a general structure shared by all mucins: a blocky polypeptide backbone comprised of terminal moieties for binding surfaces or crosslinking and a characteristic glycosylated bottlebrush. Inspired by this adaptable structure, we have created a mucin analogue platform which engenders key structural features preserved among native mucins. We have emulated the mucinous bottlebrush with a lysine-rich elastin-like polypeptide backbone, which provides primary amines for conjugation of synthetic polymer "bristles." Binding modules target surfaces of interest, to facilitate intramolecular associations, or to direct surface conformation of our construct. To demonstrate the application of our platform to clinically-relevant problems, we have tailored our mucin analogues to osteoarthritis and kidney stone disease, conditions infamous for profound morbidity and high prevalence. We will demonstrate that collagen-targeted mucin analogues adsorb to model surfaces and prevent protein fouling. This recapitulates the function of lubricin, a mucin downregulated in osteoarthritis. Similarly, we will show that we can target mineral surfaces relevant in kidney stone disease by exchanging the binding module of our analogue mucins. We will show that these altered analogues also inhibit protein-fouling, which is implicated in stone growth. In this platform technology, we have been inspired by the diverse functions of native mucins. By harnessing the general structure which gives rise to these properties, we endeavor not only to replicate the in vivo function of mucins, but also to harness the properties of natural mucins and apply them to systems not naturally protected by mucinous coatings, such as inhibiting the growth of kidney stones.

8:40am **BI+AS+NS-MoM-2 Investigation of the Mechanical and Dielectric Properties of Bone Scaffolds***, **Kimberly Cook-Chennault**,* Rutgers University

Despite the vast number of biomaterials and synthesis technologies available to treat bone defects and disease, few are readily employed for clinical use due in part to challenges in the development of materials that functionally mimic and facilitate the hierarchal processes of bone healing and regeneration. Calcium phosphate based bone replacement materials have been developed over the years for bioengineered bone structures due to their ability to mimic the general properties of mineralized bone. These bone replacement materials have mainly be fabricated in the form of hydroxyapatite (Hap), which can suffer from premature fracture when subjected to typical human load conditions. On the other hand, it is well known that enhanced osteobonding and bone growth results from the exposure of the bone to polarized Hap, which presents a negatively charged surface. Composite hydroxyapatite (Hap) – barium titanate scaffold materials are compared and contrasted with hydroxyapatite (Hap) samples for mechanical elastic moduli, compression strength and dielectric properties. Composite structures were observed to present better mechanical and dielectric properties when compared to HaP samples. For example, the elastic modulus of the HaP and composite samples were 2655.4 MPa and 3559.1 MPa, respectively. Understanding the interrelationship between scaffold architecture/material composition and mechano-transduction will improve our ability to realize patient specific solutions that eliminate hindrances to bone healing such as, lack of vascularization and lack of adequate mechanical stability.

9:00am **BI+AS+NS-MoM-3 Bioelectronics with Graphene and Graphene-Based Hybrid-Nanomaterials – From Transparent to Fuzzy Interfaces***, **Tzahi Cohen-Karni**,* Carnegie Mellon University **INVITED**

We focus on developing a new class of nanoscale materials and novel strategies for the investigation of biological entities at multiple length scales, from the molecular level to complex cellular networks. Our highly flexible bottom-up nanomaterials synthesis capabilities allow us to form unique hybrid-nanomaterials. Recently, we have demonstrated highly-controlled synthesis of 3D out-of-plane single- to few-layer fuzzy graphene (3DFG) on a Si nanowire (SiNW) mesh template. By varying graphene growth conditions, we control the size, density, and electrical properties of the NW templated 3DFG (NT-3DFG). This flexible synthesis inspires formation of complex hybrid-nanomaterials with tailored optical and electrical properties to be used in future applications such as biosensing, and bioelectronics. Currently, we target the limits of cell-device interfaces using out-of-plane grown 3DFG, aiming at electrical recordings with subcellular resolution (<5µm). Moreover, NT-3DFG unique optical properties allows formation of remote interfaces with tissue and cells. We demonstrate photostimulation of tissue and cells by using the photothermal effect of NT-3DFG. Last, we have developed a unique transparent graphene-based electrical platform that enables concurrent electrical and optical investigation of ES-derived cardiomyocytes' intracellular processes and intercellular communication. In summary, the exceptional synthetic control and flexible assembly of nanomaterials provide powerful tools for fundamental studies and applications in life science, and open up the potential to seamlessly merge either nanomaterials-based platforms or unique nanosensor geometries and topologies with cells, fusing nonliving and living systems together.

9:40am **BI+AS+NS-MoM-5 Experimental Observation of Multiple Plasmon Induced Transparency and Fano Resonance in Titanium Nitride Based Devices***, J Asencios, **Arturo Talledo**, R Moro, C Luyo,* Facultad De Ciencias Universidad Nacional De Ingeniería, Perú

Abstract: We built three types of plasmonic structures based on titanium nitride thin films by using the technique dc magnetron sputtering and D-shaped prisms as substrates. The prisms were made of glass or sapphire. Devices with structure Prism/TiN, Prism/TiN/SiO_2 and Prism/TiN/SiO_2/Nb_2O_5 were called devices type 1, type 2 and type 3, respectively. Attenuated Total Reflection in the Kretschmann configuration was studied in the three types of devices. Experimental angular spectra were fitted by using a calculation program based on the solutions to Maxwell equations. ATR spectra of devices type 1 show a wide absorption band. The main feature for ATR spectra of devices type 2 was a series of maxima and minima of reflectance within a wide absorption band. ATR spectra of devices type 3 are identified with a very sharp window within the absorption band. The spectra of devices type 2 and type 3 were associated with the phenomena of Multiple Plasmon Induced Transparency (MPIT) and Fano Resonance, respectively. Based on calculations of the square of the electric fields in the involved media, we proposed some simple phenomenological explanations for the phenomena of MPIT and Fano resonance. Potential use of these structures as refractive-index sensors was also discussed.

10:00am **BI+AS+NS-MoM-6 Breaking the Mass Resolution Limit of Shear Wave Resonators in Liquid through Integrated Microfluidic Channels***, Z Parlak, S Zhao, D French, **Stefan Zauscher**,* Duke University

Acoustic shear wave resonator sensors (SWRS), e.g., quartz crystal microbalance, are widely used in applications (e.g., thin film deposition) where their high quality factor in air or vacuum provides exquisite mass resolution. SWRS are also used as biosensors in liquid environments; however, they have not yet found widespread use outside the research environment despite their simple and robust detection modality. This is because current SWRS suffer from viscous contributions to shifts in resonance frequency, which inherently leads to low mass resolution. Furthermore, current SWRS require accurate temperature control and use large liquid volumes (~ml). Together these limitations prohibit accurate and economic measurement of surface bound mass, e.g., in protein binding assays. We show through experiments and simulations that by confining fluid into small, rigid channels oriented perpendicularly to the shear direction of the SWRS, we can manipulate liquid to behave as a lossless layer and thus perform precise mass measurements of the confined liquid. Canceling viscous effects in µ-fluidic SWRS not only enhances their mass resolution in liquid to levels observed in air/vacuum, but also enables efficient device miniaturization. Combined with the extremely small volume requirements for sensing (~nL), we show that µ-fluidic SWRS can overcome current barriers for their widespread use in diagnostic sensing and point of care applications.

10:40am **BI+AS+NS-MoM-8 Designing Anti-Fouling Lubricious Surfaces Based on Modular Approaches***, T Galhenage, C Khatri, A Vena, A Labak, T Banks, G Tremelling, **Philseok Kim**,* Adaptive Surface Technologies, Inc. **INVITED**

Biofouling, the growth of marine organisms on man-made structures, poses numerous challenges including >$15 billion additional fuel costs to vessel operators worldwide, cost and time for cleaning, corrosion issues, and negative environmental impacts. Anti-fouling coatings are the primary method of protection against this persistent problem, yet the widespread use of toxic, biocide-based coating products is causing even greater concerns for our environment and sustainability. Therefore, a groundbreaking coating solution is sought to protect both the environment and our properties.

Adaptive Surface Technologies has been developing a modular additive approach to address this problem. The SLIPS (Slippery Liquid Infused Porous Surfaces) effect (Physical module) has been successfully integrated with novel library of Surface Active Polymers (SAPs, Chemical module) to form what we call Active Performance Ingredients (APIs) that could be easily introduced as an additive in a conventional binder matrix to yield a coating formulation. I will discuss the synergistic effect of customized lubricant and SAPs in controlling biofouling without using biocides along with promising results in both laboratory and field tests. This new additive route can open up a new avenue in developing environmentally friendly, non-toxic functional additives and formulation strategies for industrial, architectural, interior, and medical coatings applications.

This work was in part funded by ARPA-E (Award no. DE-AR0000759) and completed with the generous support of the Office of Naval Research.

11:20am **BI+AS+NS-MoM-10 All Inkjet Printed Biosensor for Easy and Rapid Detection of Immunoglobulin G (IgG) Protein***, **Ridwan Fayaz Hossain**, A Kaul,* University of North Texas

Protein detection biosensors are interesting tools for detecting and measuring the levels of specific proteins in biological and environmental samples, offering certain operational advantages over standard photometric methods, notably with respect to rapidity, ease-of-use, cost, simplicity, portability, and ease of mass manufacture. Although inkjet printed electrode based sensor is widely reported, the number of fully inkjet printed biosensors is still limited [1,2]. Here, we report the design, fabrication, and evaluation of a flexible field-effect transistor (FET) for biosensing based on the inkjet printing technique, where the insulator layer is uniquely functionalized for Immunoglobulin G (IgG) protein detection. IgG is a plasma-cell protein that is produced within the lymph nodes, spleen, bone marrow, respiratory tract mucosa, tissue, etc. Since IgG protein is produced as part of the body's response to bacteria, viruses, and tissue antigens, measurement of blood IgG levels can reveal any of the body's abnormal conditions. Until now, proteins are detected mostly by antibodies in analytical formats like ELISA, immunobead assay, western blotting, and microarrays, etc. but their performance is limited by low sensitivity. This new generation biosensor is more stable and well adapted to the conditions of real samples. The protein detection biosensor reported here represents an important starting point for the design and fabrication of flexible, rapid detection biosensing devices by inkjet printing. This work shows a promising aspect of protein detection that will pave the way for the development of a fully functional device for point-of-care diagnosis.

Reference:

[1] Jensen, G. C., Krause, C. E., Sotzing, G. A., & Rusling, J. F. (2011). Inkjet-printed gold nanoparticle electrochemical arrays on plastic. Application to immunodetection of a cancer biomarker protein. Physical Chemistry Chemical Physics, 13(11), 4888-4894.

[2] Carvajal, S., Fera, S. N., Jones, A. L., Baldo, T. A., Mosa, I. M., Rusling, J. F., & Krause, C. E. (2018). Disposable inkjet-printed electrochemical platform for detection of clinically relevant HER-2 breast cancer biomarker. Biosensors and Bioelectronics, 104, 158-162.

11:40am **BI+AS+NS-MoM-11 Biosensing Applications of Silver Nanorods Array Fabricated by Glancing Angle Deposition (GLAD)*, Shashank Gahlaut,*** Indian Institute of Technology Delhi, India

Silver being most widely used material due to its unique electrical and optical properties. Here we have investigated biosensing properties of silver nanorods array (AgNRs) fabricated by glancing angle deposition. GLAD grown silver nanorods are found to be highly sensitive and selective for hydrogen sulfide (H_2S) gas. Color and water wetting (contact angle) of AgNRs array are parameters affected in the presence of this gas. H_2S is one the major gaseous products evolved in bacterial metabolic process. On the basic of H_2S production, we have shown the detection of viability as well as antibiotic resistance in different strains of bacteria.

Another potential application of as synthesized AgNRs array in Surface enhanced Raman scattering (SERS) based detection. The dengue is a viral disease and a serious global health concern. About 2.5 billion of world’s population has been living at the risk of dengue infection. It causes a spectrum of illness ranges from acute febrile illness called dengue fever (DF) to more severe life threatening forms dengue hemorrhagic fever (DHF) and dengue shock syndrome (DSS) causing vascular leakage that may lead to death. So far, neither specific treatment nor effective vaccine available for the prevention and treatment. Therefore, early detection is the key of the survival of the patients. The earlier symptom starts with mild dengue fever, at this stage the concentration of the biomarkers are very less which pose a problem in early detection. In the present study, we have demonstrated the detection of dengue from clinical blood samples employing AgNRs array as SERS substrates with hand held Raman spectrometer. A notable change in SERS spectral signature observed in the blood of dengue infected patients in comparison to that of healthy subject. This change was further confirmed using the statistical tool principal component analysis (PCA) and the samples were differentiated as healthy, dengue positive and dengue negative. All the blood samples were also dually verified with Antigen (NS1) as well as Antibody (IgM) ELISA kit. This method provides a field deployable, rapid diagnosis of dengue at its early stage.

Biomaterial Interfaces Division
Room A120-121 - Session BI+AS-MoA

Cutting Edge Bio: Bio-Nano, Bio-Energy, 3D Bio

Moderators: Heather Canavan, University of New Mexico, Jordan Lerach, ImaBiotech Corp.

1:40pm **BI+AS-MoA-1 Emulsion-templated Asymmetric Vesicles*, Laura Arriaga,*** University of Madrid, Spain **INVITED**

A vesicle is a naturally existing or an artificially prepared aqueous droplet stabilized by an amphiphilic membrane that ensures retention of hydrophilic ingredients within its core. This amphiphilic membrane typically comprises two leaflets, which have either identical or different compositions. While membranes comprising two compositionally identical leaflets exhibit lateral asymmetries or domains if prepared from mixtures of amphiphilic molecules capable of phase separation, membranes comprising compositionally different leaflets are asymmetric in the transversal direction. Moreover, internal vesicle asymmetries can be induced through the phase separation of sufficiently concentrated polymer solutions encapsulated in the vesicle cores. All these types of asymmetry dictate vesicle properties, making them more suitable than symmetric vesicles for a wide range of applications, especially to appropriately mimic biological cells. However, the utility of these vesicles depends critically on the degree of control achieved over their properties in the fabrication process. Here, we address the adequacy of emulsion droplets with well-controlled topologies, fabricated with exquisite control by microfluidic technologies, as vesicle templates. In particular, we describe a first strategy to fabricate vesicles with symmetric membranes exhibiting lateral domains and internal asymmetries using double emulsion drops as templates [1,2], and a second strategy to form vesicles with asymmetric membranes using triple emulsion drops as templates [3]. These strategies efficiently encapsulate ingredients within the core of the vesicles or their membranes and yield vesicles with monodisperse sizes and controlled degrees of asymmetry.

[1] L.R. Arriaga, S. Datta, S.-H. Kim, E. Amstad, T. Kodger, F. Monroy, D.A. Weitz. Ultra-thin shell double emulsion templated giant unilamellar lipid vesicles with controlled microdomain formation. Small 10, 950-956 (2014).

[2] J. Perrotton, R. Ahijado-Guzman, L.H. Moleiro, B. Tinao, A. Guerrero-Martinez, E. Amstad, F. Monroy, L.R. Arriaga. Microfluidic fabrication of vesicles with hybrid lipid/nanoparticle bilayer membranes. Soft Matter 15, 1388-1395 (2019).

[3] L.R. Arriaga, Y. Huang, S.-H. Kim, J.L. Aragones, R. Ziblat, S.A. Koehler, D.A. Weitz. Single-step assembly of asymmetric vesicles. Lab Chip 19, 749-756 (2019).

2:20pm **BI+AS-MoA-3 Antimicrobial Cyclic Peptide Polymer Nanopores*, Kenan Fears,*** *L Estrella,* US Naval Research Laboratory

We present a new class of bioinspired nanomaterials that are stabilized by a combination of covalent and hydrogen bonds. Prior work by others has shown that cyclic peptides can self-assemble to form supramolecular assemblies through backbone-backbone hydrogen bonding. To improve upon this molecular architecture, we develop a synthesis route to polymerize cyclic peptides and form a linear polymer chain that can transition between a rigid nanorod and a “soft” unfolded conformation. For a cyclic peptide polymer containing amine-terminated side chains on each ring, we demonstrate self-assembly can be triggered in aqueous solutions by varying the pH. We measure the elastic modulus of the rigid nanorods to be ca. 50 GPa, which is comparable to our molecular dynamics (MD) prediction (ca. 64 GPa). Our results highlight the uniqueness of our molecular architecture, namely their exemplary toughness (up to $3\ \mathrm{GJ\ m^{-3}}$), in comparison to other cyclic peptide-based assemblies. Finally, we demonstrate the amphiphilic cyclic peptide nanopores are capable of inserting into the membrane of both gram-negative and gram-positive bacteria, and causing their deaths by disrupting their osmotic pressure.

2:40pm **BI+AS-MoA-4 ToF-SIMS Analysis of the Distribution of *p*-Hydroxybenzoate in Wood*, Robyn E. Goacher,*** Niagara University*; Y Mottiar,* University of British Columbia, Canada

The progress towards a green bio-based economy depends in part on our ability to chemically modify lignocellulosic plant matter. Possible targets for such chemical modifications include ester-linked pendant groups that occur on lignin in some plant species. The lignin in poplar and willow is known to contain 1-10% of *p*-hydroxybenzoate (-*p*HB) moieties, although little is known about the function of these -*p*HB groups. To understand the function of -*p*HB, it is important to understand the distribution of -*p*HB among different cell types. Previous work with ultraviolet microscopy suggests that -*p*HB is present only in fibers and not in vessels. The goal of this work is to provide a more specific analysis of the spatial distribution of -*p*HB in wood by using surface-sensitive chemical imaging. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was used to image cross-sections of mature Lombardy poplar, juvenile (greenhouse-grown) Lombardy poplar and mature DUKE-5 willow. Lombardy poplar is known to contain higher levels of -*p*HB than the DUKE-5 willow. Samples were analyzed prior to and after solvent extraction to remove spectral interferences from small molecule extractives, which have similar chemical composition to -*p*HB and lignin. A milk alkaline hydrolysis was also performed to cleave ester-linked -*p*HB from lignin in order to confirm identification of certain peaks within the mass spectra as characteristic of -*p*HB. Multivariate statistical analysis was used to aid in the data interpretation. The process of identifying peaks that arise from -*p*HB will be discussed, and chemical images of the localization of -*p*HB will be presented. This data contributes to our understanding of how -*p*HB is distributed in wood. These insights may shed light on the role of ester-linked moieties in lignin and will hopefully advance the use of -*p*HB as a biotech target.

3:00pm **BI+AS-MoA-5 Feeling the Force; Probing the Cues that Influence Stem Cell Behaviour*, Stephanie Allen,*** School of Pharmacy, The University of Nottingham, UK **INVITED**

There is considerable research activity directed towards understanding the basic biology of stem cells and controlling their mechanisms of self-renewal and differentiation into functional tissue types. Much of the current research involves genetic and/or biochemical approaches to control proliferation and differentiation. Over the last decade, studies using biophysical approaches, including our own, have begun to impact on this understanding, revealing that physical signals and cues elaborated by neighbouring cells and the surrounding extra-cellular matrix, are also fundamental to controlling stem cell fate (1-4). For many emerging approaches/applications, including those that aim to create functioning tissues through the 3D patterning of stem cells, an understanding of such physical cues is therefore vital.

Despite this importance relatively few studies have still attempted to investigate and quantify the physical interactions between stem cells and/or the effects of applied stimuli. This talk aims to provide an overview of our recent research in this area, that aims to address this knowledge gap by utilizing force measurement approaches (including optical tweezers and atomic force microscopy). The presentation will include results from a current project where we are employing AFM-based single molecule force measurement approaches to provide new insights into the role of cadherins on mouse embryonic stem cells (mESCs).

(1) Discher *et al Science* 324 :1673-1677 (2009)

(2) Lanniel *et alSoft Matter.* 7, 6501-6514 (2011)

(3) Lanniel *et alThin Solid Films* 519, 2003-2010 (2011)

(4) Kirkham *et alScientific Reports*, 5, No. 8577 (2015)

4:20pm **BI+AS-MoA-9 Angstrom-Resolved Characterization of Electrochemical Interfaces in Real Time during Polarization*, Markus Valtiner,*** Vienna University of Technology, Austria

Electrochemical solid|liquid interfaces are critically important for energy conversion, biosensing and biodegradation processes. Yet, a real-time visualization of dynamic charging processes at electrified solid|liquid interfaces with close to atomic resolution is extremely challenging.

I will discuss a unique real-time atomistic view into dynamic charging processes at electrochemically active metal interfaces using white light interferometry in an electrochemical surface forces apparatus. This method allows simultaneous deciphering of both sides of an electrochemical interface; the solution and the metal side; with microsecond resolution under dynamically evolving reactive conditions that are inherent to technological systems in operando. The real-time capability of this approach reveals significant time lags between electron transfer, oxide reduction/oxidation, and solution side reaction during a progressing electrode process. In addition, the developed approach provides detailed insight into the structure of the electric double layer under varying charging conditions. I will also discuss how we can complementary use high resolution in-situ AFM imaging to further characterize ion layering at charged surfaces.

The presented work may have important implications for designing emerging materials utilizing electrified interfaces and may apply to bio-electrochemical processes, signal transmission and pore charging.

4:40pm **BI+AS-MoA-10 New Electrochemical Methods for Probing Metalloenzymes*, Alison Parkin,*** University of York, UK **INVITED**

Large amplitude Fourier transform alternating current voltammetry (FTacV) is being developed as a new tool for probing electron-transfer processes in metalloenzymes. We can probe non-innocent active site ligand chemistry in molybdenum enzymes and based on our new insight into the rates and energetics of electrons entering/exiting an iron sulfur cluster we have been to rationally re-design a hydrogen enzyme to increase the catalytic efficiency and hydrogen production. This talk will describe these studies and detail our solutions to the challenges in efficient data analysis and protein-electrode wiring.

Plasma Science and Technology Division
Room B130 - Session PS+AS+EM+SS+TF-MoA

Plasma-Surface Interactions

Moderators: Sebastian Engelmann, IBM T.J. Watson Research Center, Sumit Agarwal, Colorado School of Mines

1:40pm **PS+AS+EM+SS+TF-MoA-1 Cleaning Chamber Walls after ITO Plasma Etching Process*, Salma Younesy,*** *C Petit-Etienne,* LTM/CNRS, France*; S Barnola,* CEA-LETI, France*; P Gouraud,* ST Microelectronics, France*; G Cunge,* LTM/CNRS, France

Controlling the reactor walls in plasma etching is a key to avoid process drifts. In fact, the deposition of plasma generated species on the reactor walls during etching changes their chemical nature, thereby affecting plasma characteristics such as the radical concentration and the ion flux, which eventually leads to etch rates, anisotropy and selectivity variations. To overcome this issue, the chemical nature of the deposit formed on the chamber walls during etching must be determined to be able to develop efficient plasma chamber cleaning strategies. For new optoelectronic devices, the integration of materials with low volatility etch products such as ITO renders the dry cleaning processes long and laborious. Therefore, we have investigated several plasma chemistries to find out the most efficient reactor cleaning strategy after ITO etching.

The chemical nature of the reactor walls is analyzed quasi in situ by XPS using the "floating sample" technique [1], in which an Al_2O_3 sample representing the reactor walls is fixed on the 200 mm diameter wafer, but separated from it by a 4 mm gap (which forces the sample to be electrically floating even when the holding wafer is RF-biased). After the process, the wafer and sample can be transported under vacuum to the XPS analyzer and the coating formed on the walls can be analyzed (along with the cleaning efficiency).

The results show that after ITO etching the walls are contaminated by indium. At low temperature, BCl_3/Cl_2 plasma is ineffective to remove this deposit while HBr/Ar and CH_4/Cl_2 chemistries provide promising results. More particularly, an Ar-rich mixture of HBr/Ar is the most efficient strategy, which suggests that Ar^+ ions play an important role in the removal of ITO etching deposit.

[1] O. Joubert, G. Cunge, B. Pelissier, L. Vallier, M. Kogelschatz, and E. Pargon, "Monitoring chamber walls coating deposited during plasma processes: Application to silicon gate etch processes," *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.*, vol. 22, no. 3, p. 553, 2004.

2:00pm **PS+AS+EM+SS+TF-MoA-2 Plasma Resistance of Sintered Yttrium Oxyfluoride (YOF) with Various Y, O, and F Composition Ratios*, Tetsuya Goto,*** *Y Shiba, A Teramoto,* Tohoku University, Japan*; Y Kishi,* Nippon Yttrium Co., Ltd, Japan*; S Sugawa,* Tohoku University, Japan

Yttrium oxyfluoride (YOF) has been received much attention as the material for various functional components used in the plasma process chamber for semiconductor manufacturing. This is because, as compared to the widely used Y_2O_3, YOF is stable against various corrosive plasmas using halogen gases which is frequently used in the etching processes and/or chamber cleaning processes. We have reported that YOF (1:1:1) film has the higher resistance to various 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 effect of ion bombardment on the surface structure of sintered yttrium oxyfluoride (YOF) with various Y, O, and F composition ratios. By combining the starting materials of YOF, $Y_5O_4F_7$, and YF_3 in sintering, the YOF samples with different Y, O, and F composition ratios were prepared. In these samples, the oxygen composition ratio was changed from 33 at% to 7at%. According to this, the fluorine composition ratio was changed from 33at% to 66at%, and thus, the samples became from Y_2O_3 rich to YF_3 rich. Ar ion beam with 500 eV was irradiated to these YOF samples. It was found that the sputtering etching rate was monotonically decreased as the oxygen composition ratio was decreased. It was also found that the surface roughness was relatively smaller for the samples with the composition ratios of Y:O:F=1:1:1 and 5:4:7 (both correspond to the stable composition) than those with other composition ratios. The results indicated that the atomic composition ratio is an important parameter to obtain YOF with good stability against plasmas.

Acknowledgement

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

1. Y. Shiba, A. Teramoto, T. Goto, Y. Kishi, Y. Shirai and S. Sugawa, J. Vac. Sci. Technol. A, 35 (2), 021405 (2017).

2. A. Teramoto, Y. Shiba, T. Goto, Y. Kishi and S. Sugawa p. 16, AVS 65th International Symp., Long Beach, 2019.

2:20pm **PS+AS+EM+SS+TF-MoA-3 Understanding Atomic Layer Etching: Thermodynamics, Kinetics and Surface Chemistry*, Jane P. Chang*[1]*,*** University of California, Los Angeles **INVITED**

The introduction of new and functionally improved materials into silicon based integrated circuits is a major driver to enable the continued down-scaling of circuit density and performance enhancement in analog, logic, and memory devices. The top-down plasma enhanced reactive ion etching has enabled the advances in integrated circuits over the past five decades; however, as more etch-resistive materials are being introduced into these devices with more complex structures and smaller features, atomic level control and precision is needed in selective removal of these materials. These challenges point to the growing needs of identifying and developing viable etch chemicals and processes that are more effective in patterning complex materials and material systems such as multiferroics, magnetic materials and phase change materials, with tailored anisotropy and selectivity.

In this talk, a universal chemical approach is presented, combining thermodynamic assessment and kinetic validation to identify and validate the efficacy of various plasma chemistries. Specifically, potential reactions between the dominant vapor phase/condensed species at the surface are considered at various temperatures and reactant partial pressures. The volatility of etch product was determined to aid the selection of viable etch chemistry leading to improved etch rate of reactive ion etching process. Based on the thermodynamic screening, viable chemistries are tested experimentally to corroborate the theoretical prediction. Some of the above mentioned material systems such as complex oxides and metallic material systems used in logic and memory devices are used as examples to demonstrate the broad applicability of this approach.

3:00pm **PS+AS+EM+SS+TF-MoA-5 Comparison of Silicon Surface Chemistry between Photo-Assisted Etching and Ion-Assisted Etching*, Emilia Hirsch,*** *L Du, V Donnelly, D Economou,* University of Houston

Etching of p-Si in 60 mTorr Cl_2/Ar Faraday-shielded inductively coupled plasmas was investigated under both ion-assisted etching (IAE) and photo-assisted etching (PAE) conditions. Real-time etching rate and after-etch Si surface chemical composition were characterized by laser interferometry and vacuum-transfer X-ray photoelectron spectroscopy (XPS), respectively. By varying the duty cycle of a pulsed negative DC bias applied to the sample stage, it was found that the IAE rate scaled with the ion current integrated over the bias period, and the total etching rate was simply the sum of PAE and IAE rates. Consequently, little or no synergism occurred between VUV photon- and ion-bombardment stimulated etching. The PAE rate was ~ 210 nm/min at 60 mTorr. Above the 25 eV threshold, the IAE etching rate increased with the square root of the ion energy. Compared to RF bias, a more monoenergetic IED was obtained by applying pulsed DC bias, allowing precise control of ion energy near the low-energy IAE threshold. XPS spectra showed that, when compared to IAE, the chlorinated layer on the surface of samples etched under PAE conditions had significantly lower chlorine content, and it was composed of SiCl only. Under IAE conditions, however, Si· dangling bonds, $SiCl_2$, and $SiCl_3$ were found, in addition to SiCl, with relative abundance of $SiCl>SiCl_2>SiCl_3$. The absence of higher chlorides and Si· dangling bonds under PAE conditions suggested that VUV photons and ions are interacting with the Si surface

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[1] **PSTD Plasma Prize Winner**

very differently. When PAE and IAE occurred simultaneously, energetic ion bombardment dictated the surface chemistry that resulted in the formation of higher chlorides.

3:20pm **PS+AS+EM+SS+TF-MoA-6 Chemical Reaction Probabilities in the Etching of Si by Fluorine Atoms Produced in a Mixture of NF-$_3$/SF$_6$ Plasma***, **Priyanka Arora**[1], T Nguyen,* University of Houston*; S Nam,* Samsung Electronic Company, Republic of Korea*; V Donnelly,* University of Houston

Reaction probabilities in the absence of ion bombardment, defined as the number of silicon atoms removed per incident fluorine atom, have been investigated in mixtures of NF_3 and SF_6 plasmas in an inductively-coupled plasma reactor. Fluorine atom densities were measured by optical emission actinometry, and isotropic etching rates were measured by the degree of undercutting of SiO_2-masked silicon, using cross-sectional scanning electron microscopy (SEM). In addition, atomic force microscopy (AFM) was used to examine surface roughness after etching. The F atom reaction probabilities derived from these measurements indicate ~30-fold higher reaction probability in SF_6 plasma compared with values in NF_3 plasma. Surfaces etched in SF_6 plasma were much smoother than those etched in NF_3 plasma. Addition of only 10% SF_6 to an NF_3 plasma produced a much higher reaction probability (~10-fold) than in a pure NF_3 plasma. This surprising enhancement of reaction probabilities for F with Si in SF_6 plasma will be shown to be due to adsorbed sulfur acting as a catalyst to greatly enhance the etching rate of Si. By allowing sulfur in isopropyl alcohol to evaporate on the masked Si samples, sulfur could be preferentially deposited in relatively high concentrations near mask edges in ~2 mm diameter periodic "strings of beads". When this sample is placed side by side with one not exposed to sulfur, the sulfur dosed sample etched several times faster at the center of each bead, while sulfur-free surface exhibited the expected slower rate.

4:00pm **PS+AS+EM+SS+TF-MoA-8 John Thornton Memorial Award Lecture: Low Temperature Plasma-Materials Interactions: Foundations of Nanofabrication And Emerging Novel Applications At Atmospheric Pressure***, **Gottlieb S. Oehrlein**[2],* University of Maryland, College Park **INVITED**

Our ability to understand and control the interactions of non-equilibrium plasma with surfaces of materials has been an exciting frontline and enabled the realization of new applications and technologies. The plasma-surface interactions (PSI) field has grown rapidly because of a number of reasons. First, plasma-assisted etching (PE) is one of the foundations of micro- and nanofabrication where increasingly atomistic precision in materials processing is required. By enabling the realization of intricate material features that semiconductor circuits and microstructures consist of, PE makes possible our technological tools that form modern society. This exceedingly complex procedure begins with the transfer of a resist mask in a directional and chemically selective fashion into various materials. Controlling profile shape, critical dimensions, surface roughness, and electrical integrity are crucial, and determined by PSI. Second, development of novel low temperature plasma sources operating at atmospheric pressure has enabled advances in areas where use of PSI has historically been limited, e.g. biology. In this talk I will present a brief review of contributions that I and my collaborators have been honored to make to our understanding of PSI, in particular in the areas of surface processes that are essential for achieving the objectives of plasma etching processes in current semiconductor fabrication that are approaching the atomic scale, and interaction of low temperature atmospheric pressure plasma sources with model polymers and biomolecules aimed at disinfection and sanitation of biological materials.

4:40pm **PS+AS+EM+SS+TF-MoA-10 Determining Surface Recombination Probabilities during Plasma-enhanced ALD using Lateral High Aspect Ratio Structures***, **Karsten Arts**,* Eindhoven University of Technology, The Netherlands, Netherlands*; M Utriainen,* VTT Technical Research Centre of Finland, Finland*; R Puurunen,* Aalto University School of Chemical Engineering, Finland*; E Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands*; H Knoops,* Eindhoven University of Technology, The Netherlands

In this work we measure surface recombination probabilities *r* of plasma radicals, which is essential for the modeling and understanding of radical-driven plasma processes. Such quantitative information on *r* is scarcely reported in the literature and typically obtained by difficult and indirect measurement techniques. Here, we determine *r* using plasma-enhanced atomic layer deposition (ALD) on high aspect ratio (AR) structures, where the AR up to which film growth is obtained gives direct insight into *r* corresponding to the growth surface. This is demonstrated by measuring the recombination probabilities of O atoms on SiO-$_2$, TiO_2, Al_2O_3 and HfO_2, revealing a surprisingly strong material-dependence. Aside from studying different materials, our method can for instance be used to investigate the impact of pressure and temperature on *r*. This can provide valuable information for e.g., device fabrication, plasma source design and simulations, in the context of plasma-enhanced ALD but also relevant outside this field.

For this study, we use microscopic lateral-high-aspect-ratio (LHAR) structures[1] supplied by VTT (PillarHall® LHAR4). These chips have extremely high AR trenches (AR<10000) such that film growth is limited up to a certain penetration depth for even the most conformal processes. In the case of plasma ALD, where the film conformality is typically limited by surface recombination,[2] we show that the achieved penetration depth can be used to determine *r*. Furthermore, the LHAR structures allow for comparison of growth behavior with and without an ion component.

These opportunities are demonstrated by plasma ALD of SiO-$_2$, TiO_2, Al_2O_3 and HfO_2, using an O_2/Ar plasma and $SiH_2(N(C_2H_5)_2)_2$, $Ti(N(CH_3)_2)_4$, $Al(CH_3)_3$ and $HfCp(N(CH_3)_2)_3$, respectively, as precursors. It is observed that an exponential increase in plasma exposure time is required to linearly increase the film penetration depth. This relation, which solely depends on *r*, has been used to determine $r=(6\pm2)\cdot10^{-5}$, $(6\pm3)\cdot10^{-5}$, $(1\text{-}10)\cdot10^{-3}$ and $(0.1\text{-}10)\cdot10^{-2}$ for oxygen radicals on SiO-$_2$, TiO_2, Al_2O_3 and HfO_2, respectively. Corresponding to these large differences in *r*, growth of SiO_2 and TiO_2 penetrated extremely deep up to AR~900, while deposition of Al_2O_3 and HfO_2 was achieved up to AR~90 and AR~40, respectively. This strong material-dependence illustrates the importance of our quantitative research on surface recombination of plasma radicals.

1. Arts, Vandalon, Puurunen, Utriainen, Gao, Kessels and Knoops, J. Vac. Sci. Technol. A **37**, 030908 (2019)
2. Knoops, Langereis, van de Sanden and Kessels, J. Electrochem. Soc. **157**, G241 (2010)

5:00pm **PS+AS+EM+SS+TF-MoA-11 Study of Plasma-Photoresist Interactions for Atomic Layer Etching Processes***, **Adam Pranda**[3], K Lin, G Oehrlein,* University of Maryland, College Park

The emergence of atomic layer etching (ALE) processes has enabled improved control of surface profiles. Whereas the implementation of ALE processes on hard mask materials has been well established, the effects of these processes on photoresist materials is not well known. With the advent of next generation extreme ultraviolet (EUV) photoresists, there is the potential to utilize ALE processes with photoresist materials for fabrication of sub-10 nm feature sizes.

The plasma processing of photoresist materials induces several key physical and chemical modifications which affect material properties such as the etching behavior and surface roughness. In this work, we utilize in-situ ellipsometry, atomic force microscopy (AFM), x-ray photoelectron spectroscopy (XPS), and Fourier transform infrared (FTIR) spectroscopy to interpret the relationships between the aforementioned material properties, the photoresist chemical composition, and plasma ALE parameters such as ion energy and precursor gas type. By comparing these relationships between baseline continuous plasma etching processes and ALE processes, which include the introduction of chemically reactive surface passivation, we elucidate the intrinsic photoresist behaviors under plasma exposure and how an ALE process specifically impacts these behaviors.

Under nonreactive plasma chemistries, a universal response among photoresist materials is the development of a surface dense amorphous carbon (DAC) layer due to energetic ion bombardment. We have found that the photoresist etch rate is inversely proportional to the DAC layer thickness.[1] However, photoresists with UV sensitive pendant groups, such as 193 nm photoresists, develop a greater surface roughness due to the stresses in the surface generated by synergistic ion and UV photon interactions.

With depositing fluorocarbon (FC)-based ALE gas chemistries, the deposited FC layer reacts with the DAC layer and converts it into a mixed layer. This incorporation of FC into the DAC layer reduces the surface

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

[2] **John A. Thornton Memorial Award Winner**

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

roughness without impacting the etch rate of the underlying photoresist as long as a sufficient DAC layer thickness remains.[2] This behavior is potentially advantageous for maximizing the photoresist to SiO_2 selectivity while maintaining an adequate surface roughness.

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[1] A. Pranda et al., J. Vac. Sci. Technol. A **36**, 021304 (2018).

[2] A. Pranda et al., Plasma Process. Polym. e1900026 (2019).

New Challenges to Reproducible Data and Analysis Focus Topic

Room A211 - Session RA+AS+NS+SS-MoA

Quantitative Surface Analysis II/Big Data, Theory and Reproducibility

Moderators: Kateryna Artyushkova, Physical Electronics, Donald Baer, Pacific Northwest National Laboratory

1:40pm **RA+AS+NS+SS-MoA-1 A Data-Centric View of Reproducibility*,* *Anne Plant,*** National Institute of Standards and Technology (NIST)*; J Elliott,* NIST*; R Hanisch,* National Institute of Standards and Technology (NIST) **INVITED**

Ideally, data should be shareable, interpretable, and understandable within the scientific community. There are many challenges to achieving this, including the need for high quality documentation and a shared vocabulary. In addition, there is a push for rigor and reproducibility that is driven by a desire for confidence in research results. We suggest a framework for a systematic process, based on consensus principles of measurement science, to guide researchers and reviewers in assessing, documenting, and mitigating the sources of uncertainty in a study. All study results have associated ambiguities that are not always clarified by simply establishing reproducibility. By explicitly considering sources of uncertainty, noting aspects of the experimental system that are difficult to characterize quantitatively, and proposing alternative interpretations, the researcher provides information that enhances comparability and reproducibility.

2:20pm **RA+AS+NS+SS-MoA-3 Enhancing Data Reliability, Accessibility and Sharing using Stealthy Approaches for Metadata Capture*,* *Steven Wiley,*** Pacific Northwest National Laboratory **INVITED**

Science is entering a data-driven era that promises to accelerate scientific advances to meet pressing societal needs in medicine, manufacturing, clean energy and environmental management. However, to be usable in big data applications, scientific data must be linked to sufficient metadata (data about the data) to establish its identity, source, quality and reliability. This has also driven funding agencies to require projects to use community-based data standards that support the FAIR principles: Findable, Accessible, Interoperable, and Reusable. Current concerns about data reproducibility and reliability have further reinforced these requirements. Truly reusable data, however, requires an enormous amount of associated metadata, some which is very discipline and sample-specific. In addition, this metadata is typically distributed across multiple data storage modalities (e.g. lab notebooks, electronic spreadsheets, instrumentation software) and is frequently generated by different people. Assessing and consolidating all of the relevant metadata has traditionally been extremely complex and laborious, requiring highly trained and motivated investigators as well as specialized curators and data management systems. This high price has led to poorly documented datasets that can rarely be reused. To simplify metadata capture and thus increase the probability it will indeed be captured, EMSL (Environmental Molecular Sciences Laboratory) has developed a general-purpose metadata capture and management system built around the popular ISA-Tab standard (Investigation-Study-Assay Tables). We have modified this framework by mapping it onto the EMSL workflow, organized as a series of "transactions". These transactions are natural points where metadata is generated, include specifying how samples will be generated and shipped, instrument scheduling, sample storage, and data analysis. Software tools have been built to facilitate these transactions, automatically capture the associated metadata and link it to the relevant primary data. This metadata capture system works in concert with automated instrument data downloaders and is compatible with commercial sample tracking and inventory management systems. By creating value-added tools that are naturally integrated into the normal scientific workflow, our system enhances scientific productivity, thus incentivizing adoption and use. The entire system is designed to be general purpose and extensible and thus should be a useful paradigm for other scientific projects that can be organized around a transactional model.

3:00pm **RA+AS+NS+SS-MoA-5 From Electrons to X-rays: Tackling Big Data Problems through AI*,* *Mathew Cherukara,*** *Y Liu, M Holt, H Liu, T Gage, J Wen, I Arslan,* Argonne National Laboratory **INVITED**

As microscopy methods and detectors have advanced, the rates of data acquisition and the complexity of the acquired data have increased, and these are projected to increase several hundred-fold in the near future. The unique electron and X-ray imaging capabilities at the Center for Nanoscale Materials (CNM) are in a position to shed light on some of the most challenging and pressing scientific problems we face today. To fully leverage the capability of these advanced instruments, we need to design and develop effective strategies to tackle the problem of analyzing the data generated by these imaging tools, especially following facility upgrades such as the upgrade to the Advanced Photon Source (APS-U) and the commissioning of the ultrafast electron microscope (UEM).

The data problem is especially acute in the context of coherent imaging methods, ultra-fast imaging and multi-modal imaging techniques. However, analysis methods have not kept pace. It is infeasible for a human to sort through the large, complex data sets being generated from imaging experiments today. At the CNM, we apply machine learning algorithms to our suite of electron and X-ray microscopy tools. Machine learning workflows are being developed to sort through data in real-time to retain only relevant information, to invert coherently scattered data to real-space structure and strain, to automatically identify features of interest such as the presence of defects, and even to automate decision making during an imaging experiment. Such methods have the potential not only to decrease the analysis burden on the scientist, but to also increase the effectiveness of the instruments, for instance by providing real-time experimental feedback to help guide the experiment.

4:00pm **RA+AS+NS+SS-MoA-8 Quantifying Shell Thicknesses of Core-Shell Nanoparticles by means of X-ray Photoelectron Spectroscopy*,* *Wolfgang Werner,*** Vienna University of Technology, Austria **INVITED**

Determining shell thicknesses and chemistry of Core-Shell Nanoparticles (CSNPs) presently constitutes one of the most important challenges related to characterisation of nanoparticles. While for particlae number concentration various routine analysis techniques as well as methods providing reference measurements have been or are in the process of being developed, one of the most promising candidates for shell thickness determination is x-ray photoelectron spectroscopy (XPS).

Different approaches to quantify shell thicknesses will be presented and compared. These comprise: (1) The infinitesimal columns model (IC), (2) Shard's empirical formula (TNP-model) and (3) SESSA (Simulation of Electron Spectra for Surface Analysis) simulations with and (4) without elastic scattering.

CSNP XPS intensities simulated with SESSA for different combinations of core/shell-material combinations for a wide range of core and shell thicknesses have been evaluated with the TNP-model and the retrieved thicknesses are in good agreement with the nominal thickness, even when elastic scattering is turned on during the simulation, except for pathological cases. For organic shell materials these simulations fully confirm the validity of the (much simpler) TNP-method, which also coincides with the IC model.

Experimental data on of a round robin experiment of PMMA@PTFE CSNPs involving three research institutions were analysed with the aforementioned approaches and show a good consistency in that evaluations of the shell thicknesses among the institutions agree within 10% (and are in good agreement with the nominal shell thickness). This consistency is promising since it suggests that the error due to sample preparation can be controlled by following a strict protocol.

Use of the F1s signal leads to significant deviations in the retrieved shell thickness. Independent measurements using Transmission Electron Microscopy were also performed, which revealed that the core-shell structure is non-ideal, i.e. the particles are aspherical and the cores are acentric within the particles. SESSA simulations were employed to estimate the effect of various types of deviations of ideal NPs on the outcome of shell thickness determination.

The usefulness and importance of different kind of electron beam techniques for CSNP analysis and in particular shell thickness determination is discussed.

4:40pm **RA+AS+NS+SS-MoA-10 Modeling the Inelastic Background in X-ray Photoemission Spectra for Finite Thickness Films***, **Alberto Herrera-Gomez**,* CINVESTAV-Unidad Queretaro, México

The background signal in photoemission spectra caused by inelastic scattering is usually calculated by convolving the total signal with the electron-energy loss-function. This method, which was proposed by Tougaard and Sigmund in their classic 1982 paper [1], only works (as clearly indicated in [1]) for homogeneous materials. However, the method is commonly applied to finite thickness films. In this paper it is going to be described the proper way to remove the inelastic background signal of spectra from thin-conformal layers including buried layers and delta-doping [2]. The method is based on the straight-line inelastic scattering path, which is expected to be a very good approximation for low energy losses (near-peak regime). It is also a common practice to use the parametric Tougaard Universal Cross Section [3] with the provision that, instead of using the theoretical values for the parameters valid for homogeneous materials, the B-parameter is allowed to vary until the experimental background signal ~ 50 to 100 eV below the peak is reproduced. This is equivalent to scale the loss-function, which partially compensates the error from using the convolution method [1]. The error compensation on the modeling of the background of finite-thickness layers by scaling the loss-function will be quantitatively described.

[1] 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.

[2] A. Herrera-Gomez, The photoemission background signal due to inelastic scattering in conformal thin layers (Internal Report), 2019. http://www.qro.cinvestav.mx/~aherrera/reportesInternos/inelastic_background_thin_film.pdf.

[3] S. Tougaard, Universality Classes of Inelastic Electron Scattering Cross-sections, Surf. Interface Anal. 25 (1997) 137–154. doi:10.1002/(SICI)1096-9918(199703)25:3<137::AID-SIA230>3.0.CO;2-L.

5:00pm **RA+AS+NS+SS-MoA-11 R2R(Raw-to-Repository) Characterization Data Conversion for Reproducible and Repeatable Measurements***, **Mineharu Suzuki**, H Nagao, H Shinotsuka,* National Institute for Materials Science (NIMS), Japan*; K Watanabe,* ULVAC-PHI Inc., Japan*; A Sasaki,* Rigaku Corp., Japan*; A Matsuda, K Kimoto, H Yoshikawa,* National Institute for Materials Science (NIMS), Japan

NIMS, Japan, has been developing a materials data platform linked with a materials data repository system for rapid new material searching by materials informatics. The data conversion from raw data to human-legible/machine-readable data file is one of the key preparation techniques prior to data analysis, where the converted data file should include meta-information. Our tools can convert raw data to a structured data package that consists of (1) characterization measurement metadata, (2) primary parameters which we will not call "metadata" to distinguish from (1), (3) raw parameters as written in original raw data, and (4) formatted numerical data. The formatted numerical data are expressed as matrix type with robust flexibility, not obeying a rigid definition. This flexibility can be realized by applying the data conversion style of Schema-on-Read type, not Schema-on-Write type based on *de jure* standards such as ISO documents. The primary parameters are carefully selected from raw parameters and their vocabularies are replaced from instrument-dependent terms to general ones that everyone can readily understand. These primary parameters with linked specimen information are useful for reproducible and repeatable instrument setup. By this R2R conversion flow, we have verified that we can generate and store interoperable data files of XPS spectra and depth profiles, powder XRD patterns, (S)TEM images, TED patterns, EELS spectra, AES spectra, EPMA spectra and elemental mapping, and theoretical electron IMFP data. We have also developed a system to allow semi-automatic data transfer from an instrument-controlling PC isolated from the network, by adopting a Wi･Fi-capable SD card's scripting capability, while keeping the PC offline. We are working on further software development for on-demand data manipulation after R2R data conversion. So far it has been possible to perform XPS peak separation using automated information compression technique. Using these components, high-throughput data conversion/accumulation and data analyses are realized, where human interaction is minimized. Using metadata extracted from raw data, other users can reproduce or repeat measurements even if they did not carry out the original measurement. Human-legible and machine-readable numerical data is utilized for statistical analyses in informatics.

2D Materials
Room A216 - Session 2D+AS+MI+NS-TuM
2D Materials Characterization including Microscopy and Spectroscopy

Moderator: David Geohegan, Oak Ridge National Laboratory

8:00am **2D+AS+MI+NS-TuM-1 Near-field Infrared Spectroscopy of Single Layer $MnPS_3$***,* ***Sabine Neal,*** University of Tennessee Knoxville*; H Kim,* Rutgers University*; K Smith, A Haglund, D Mandrus,* University of Tennessee Knoxville*; H Bechtel,* Advanced Light Source, Lawrence Berkeley National Laboratory*; L Carr,* National Synchrtoron Light Source II, Brookhaven National Lab*; K Haule, D Vanderbilt,* Rutgers University*; J Musfeldt,* University of Tennessee Knoxville

In order to explore the properties of a complex van der Waals material under confinement, we measured the near-field infrared response of the magnetic chalcogenide $MnPS_3$ in bulk, few-, and single-layer form and compared the results with traditional far field vibrational spectroscopy and complementary lattice dynamics calculations. Trends in the activated B_u mode near 450 cm^{-1} are particularly striking, with the disappearance of this structure in the thinnest sheets. Combined with the amplified response of the A_g mode and analysis of the $A_u + B_u$ features, we find that the symmetry is unexpectedly *increased* in single-sheet $MnPS_3$. The monoclinicity of this system is therefore a consequence of the long-range stacking pattern rather than local structure.

8:20am **2D+AS+MI+NS-TuM-2 Multi-parameter Analysis of Genesis and Evolution of Secondary Electrons produced in the Low Energy Regime***,* ***Alessandra Bellissimo,*** ETH Zürich, Switzerland*; G Pierantozzi,* CNR - Istituto Officine Materiali, Italy*; A Ruocco, G Stefani,* Università degli Studi Roma Tre, Italy*; O Ridzel, V Astašauskas, W Werner,* Technische Universität Wien, Austria*; M Taborelli,* CERN, Switzerland*; G Bertolini, U Ramsperger,* ETH Zürich, Switzerland*; O Gürlü,* ETH Zürich, Switzerland, Turkey*; D Pescia,* ETH Zürich, Switzerland

The mechanisms responsible for electron-induced Secondary Electron Emission (SEE) generation of these ubiquitous Secondary Electrons (SEs) in a solid surface is not yet fully understood. In particular, the question *how many* "true secondary" electrons are generated and emitted from the target per incident primary electron awaits resolution and is of great fundamental as well as technological importance. The present work reports on a study of these and related questions by means of a variety of spectroscopic tools of increasing finesse. The interaction of Low-Energy Electrons with surfaces exhibiting different long-range order, was investigated by combining measurements of the Total Electron Yield in absolute units, single-electron as well as (e,2e)-coincidence spectroscopy. This investigation has led to the disentanglement of the elementary processes that need to be considered and comprehended for the understanding of the SE-generation probability, fully taking into account both energy and momentum conservation in the collision and the band structure of the solid. Single ionising scattering events, assisted by collective excitations, i.e. *plasmons*, constitute one of the fundamental ingredients leading to SEE. In the Low-Energy-regime the electron yield of a material is constituted by the interplay of reflectivity and SEE, both strongly dictated by the target band structure. The gathered information is further used in an attempt to interpret the signal generation mechanisms relevant in Scanning Field-Emission Microscopy (SFEM) [1].

Reference:

[1] A. Bellissimo, PhD Thesis, *"Multiparameter Analysis of Genesis and Evolution of Secondary Electrons produced in the Low Energy Regime"*, URL:

https://www.researchgate.net/publication/332684398_Multiparameter_Analysis_of_Genesis_and_Evolution_of_Secondary_Electrons_produced_in_the_Low_Energy_regime

8:40am **2D+AS+MI+NS-TuM-3 Probing Point Defects, Folds and Interfaces in 2D Material Heterostructures using Scanning Transmission Electron Microscopy***,* ***Sarah Haigh,*** University of Manchester, UK **INVITED**

Scanning Transmission Electron Microscopy (STEM) is one of the few techniques able to probe the structure and chemistry of 2D materials when these are stacked to form vertical heterostructures. By combining STEM with electron energy loss spectroscopy and energy dispersive X-ray spectroscopy it is possible to characterise individual point defects,[1] to measure interlayer distances for dissimilar materials [2] and to investigate the microstructure of mechanically deformed structures at the atomic scale [3]. We have extensively employed plan view and cross sectional STEM imaging to investigate complex 2D heterostructures. For example, we have shown that protruding defects prevent the realisation of pristine interfaces between transition metal selenides (MoSe2, WSe2, NbSe2) and boron nitride, unless exfoliation is performed in an inert environment.[2]

We have analysed microstructures produced when 2D van der Waals materials (graphite, boron nitride, MoSe2) are subjected to mechanical deformation and find that the types of defect can be predicted from just the bend angle and thickness of the materials.[3] In particular we find that above a critical thickness the materials exhibit numerous twin boundaries and for large bend angles these can contain nanoscale regions of local delamination. Such features are proposed to be important in determining how easily the material can be thinned by mechanical or liquid exfoliation.[3]

2D material heterostructures are also enabling new STEM imaging capabilities. We show they can be used as a platform to study real time reactions in liquid environments with unprecedented spatial resolution and spectroscopic capabilities [4]. We further demonstrate that graphene encapsulation allows imaging of point defect dynamics, structural degradation and mechanically induced stacking faults in 2D monochalcogenides, GaSe and InSe [1].

References

[1] D G Hopkinson et al, ACS Nano, (2019) 10.1021/acsnano.8b08253

[2] A P Rooney et al. Nano Letters, (2017) 17, 5222.

[3] A P Rooney et al. Nature Communications (2018) 9, 3597

[4] D J Kelly et al Nano Letters, (2018) 18, 2, 1168

9:20am **2D+AS+MI+NS-TuM-5 Low-Energy Electron Induced Disordering and Decomposition of Self-assembled Monolayers on Au(111)***,* ***Jodi Grzeskowiak***[1]*,* University at Albany - SUNY*; C Ventrice, Jr.,* SUNY Polytechnic Institute

To study the interaction of low energy electrons with thin organic films, measurements have been performed on electron induced disordering and decomposition of 1-decanethiol molecules grown via vapor phase deposition on Au(111). Surface analysis techniques were used to characterize the monolayers before and after electron exposure. LEED was used to determine the structure of the SAM and the rate of disordering and decomposition. It was observed that the diffraction pattern of the lying down phase of the SAM, held near 100 K, almost completely disappears within about three minutes of exposure. However, when the temperature of the irradiated sample was raised to 300 K and then cooled back down to around 100 K, most of the intensity of the diffraction pattern returns, indicating that electron exposure is primarily inducing disorder. TPD was used to evaluate the thermal stability of the SAMs and the resulting desorption products after electron exposure. For the standing up phase SAM, two desorption features for the hydrocarbon fragments of the SAM are observed, one around 130 °C and a second near 220 °C. For the lying down phase, only the higher temperature desorption feature is observed, which indicates that the SAM is converting from the standing up phase to the lying down phase during the heating process. For both phases, desorption peaks for S and H_2S at around 250 °C were observed, suggesting that there is a high probability for the alkane chain of the decanethiol molecule to detach from the sulfur head group. After electron exposure of the standing up phase, a large reduction in the intensity of the two desorption peaks for the masses monitored for the hydrocarbon fragments was observed. However, the intensities of the peaks associated with S and H_2S were similar to those for the samples that were not irradiated with electrons. For the lying down phase, the intensities and positions of all of the desorption peaks were similar to the unexposed SAMs, which indicates that the cross-section for electron beam damage for the lying down phase is much lower than that for the standing up phase. Ex-situ XPS was used to monitor the decomposition of the SAMs. After irradiation with 80 eV electrons, an uptake of oxygen was observed in the XPS measurements for both samples. This oxygen uptake gives evidence that oxygen in the air is reacting with carbon and sulfur atoms whose bonds were broken during electron exposure.

9:40am **2D+AS+MI+NS-TuM-6 Continuous Silicene, Silicene Ribbons and Surface Reconstructions on h-$MoSi_2$***,* ***Anna Costine****, C Volders,* University of Virginia*; M Fu,* Oak Ridge National Laboratory*; P Reinke,* University of Virginia

Silicene has emerged as a 2D material of interest because of its spin -orbit coupling, tunable electronic structure, and Dirac type behavior. Synthesis of silicene with preserved Dirac-type electronic structure has proven

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[1] **ASSD Student Award Finalist**

challenging, but is critical to realizing theoretically predicted quantum states and devices. To date, Ag(111) remains the most popular substrate for silicene synthesis, but is discussed controversially due to its similarity with surface alloys. Silicene has also been synthesized on other substrates including Ir, $IrSi_3$, and ZrB_2. Silicene synthesis on a semiconducting substrate with a low buckling conformation to conserve the Dirac-type behavior would be ideal. The synthesis of silicene on new substrates that allow for direct device integration is an important next step.

We developed an alternate approach to silicene synthesis that allows for silicene synthesis on semiconducting silicides. The (0001) surface of h-MoSi2 has hexagonal symmetry and a lattice constant close to that of silicene. Our recent measurements support the assumption that silicene is electronically decoupled from the substrate. The h-MoSi2 crystallites, which are terminated by the (0001) plane are grown by depositing Mo onto a Si (001) or Si(111) surface. Upon annealing to ~800℃, the Si atoms decouple from the underlying surface and form a weakly buckled silicene layer with the √3 x√3 surface as seen by STM.

Our recent work expands this study and uses STM/S at 77 K to achieve a comprehensive description of silicene-on-silicide. The amount of Mo deposited (0.3 nm - 18 nm) and annealing temperature (700- 1000℃) were varied. All surface structures discussed here are on h-MoSi2 crystallites in the (0001) plane,. Three distinct surface structures coexist - silicene ribbons , a 4x4 reconstruction, and a complex reconstruction which is very sensitive to variations in the bias voltage. The electronic structure of silicene-ribbons shows a V-shaped density of states close to EF, indicative of Dirac-like behavior, while the other reconstructions are semiconducting. The surface and electronic structures observed on h-$MoSi_2$ crystallites as a function of the synthesis conditions will be discussed. The preference for silicene-ribbons in the low T STM/STS measurements is currently attributed to a faster post-deposition cooling rate, but the exact mechanism is still open to debate. We will present a detailed discussion of the electronic structure of silicene and silicene ribbons, and suggest mechanisms for the transition from the (0001) surface to silicene. Our goal is to develop synthesis approaches suitable for device integration of both silicene conformations.

11:00am **2D+AS+MI+NS-TuM-10 Epitaxial Growth and Characterization of Single-Orientation Single-Layer Transition Metal Dichalcogenides on Au(111)***, L Bignardi,* University of Trieste, Italy*; **Daniel Lizzit,*** Elettra - Sincrotrone Trieste, Trieste, Italy*; B Harsh, E Travaglia,* Department of Physics, University of Trieste, Italy*; C Sanders,* iNANO, Aarhus University, Denmark, UK*; M Dendzik,* Aarhus University, Denmark, Germany*; P Lacovig,* Elettra-Sincrotrone Trieste, Italy*; M Michiardi,* iNANO, Aarhus University, Denmark, Canada*; M Bianchi,* Aarhus University, Denmark*; R Larciprete,* CNR-Institute for Complex Systems, Roma, Italy*; J Flege, J Falta,* University of Bremen, Germany*; P Das,* Abdus Salam International Centre for Theoretical Physics, Trieste, Italy*; J Fujii, I Vobornik,* IOM-CNR, Laboratorio TASC, Trieste, Italy*; M Ewert, L Buß,* University of Bremen, Germany*; A Baraldi,* University of Trieste, Italy*; P Hofmann,* Aarhus University, Denmark*; S Lizzit,* Elettra - Sincrotrone Trieste, Trieste, Italy

It has been widely demonstrated that Transition Metal Dichalcogenides (TMDs), and in particular MoS_2 and WS_2 could be good candidates for future electronic devices because of their intrinsic electronic properties and their potential for ultimate device scaling. In the single layer (SL) form, the inversion symmetry breaking and the strong spin-orbit coupling of the heavy transition metals (Mo or W) open new possibilities for data storage and computing thanks to the spin and valley degrees of freedom. However, in order to investigate the fundamental physics behind these materials and to produce high quality electronic devices, SL TMDs with enough large area and high quality are demanded. In particular, single domain oriented layers, that are SLs without mirror domains, allow to strongly suppress defects due to the absence of grain boundaries which are known to degrade the overall performances.

We here present a successful synthesis method based on physical vapor deposition that consists in dosing W or Mo in H_2S atmosphere onto Au(111), and provide an in-depth characterization of the synthesized SL TMDs through different surface science techniques. Synchrotron radiation based photoelectron spectroscopy in the fast modality (fast-XPS) was used to carefully tune the growth parameters whereas high resolution (HR-XPS) was used for the characterization. In particular fast-XPS allowed to optimize the growth parameters which turned out to be different for MoS_2 [1] with respect to WS_2[2]. Then, photoelectron diffraction (XPD) was employed to find the structural parameters of the SLs and to unambiguously determine their single orientation character and the relative alignment with respect to the underlying substrate. Scanning Tunneling Microscopy (STM), Low Energy Electron Diffraction (LEED) and Microscopy (LEEM) added further insight into the lateral extension of the SLs and the structural order at the atomic level.

[1] H. Bana, E. Travaglia, L. Bignardi, P. Lacovig, C. E. Sanders, M. Dendzik, M. Michiardi, M. Bianchi, D. Lizzit, F. Presel, D. D. Angelis, N. Apostol, P. K. Das, J. Fujii, I. Vobornik, R. Larciprete, A. Baraldi, P. Hofmann and S. Lizzit, 2D Materials, 2018, 5, 035012.

[2] L. Bignardi, D. Lizzit, H. Bana, E. Travaglia, P. Lacovig, C. E. Sanders, M. Dendzik, M. Michiardi, M. Bianchi, M. Ewert, L. Buss, J. Falta, J. I. Flege, A. Baraldi, R. Larciprete, P. Hofmann, and S. Lizzit, Physical Review Materials 3, 014003 (2019).

11:20am **2D+AS+MI+NS-TuM-11 Surface Reactivity of MoS_2 by ambient pressure X-ray Photoelectron Spectroscopy***, **Rafik Addou,** D Dardzinsky, G Herman,* Oregon State University

Molybdenum disulfide (MoS_2) has potential applications as a low-cost catalyst for the hydrogen evolution reaction (HER). Defect sites in MoS_2 have been demonstrated to have high catalytic activities, where edge sites and sulfur vacancies are the major active sites for HER. Intentionally inducing defects offers a simple way to enhance the reactivity of MoS_2 and other 2D materials. In this study, we have characterized the surface reactivity and the catalytic activities of bulk MoS_2 samples using ambient pressure X-ray photoelectron spectroscopy (APXPS). The pristine surface was exposed to 1 mbar of H_2O vapor for temperatures ranging from 300 to 573 K. APXPS Mo 3*d*, S 2*p*, and O 1*s* core levels do not show any significant changes under these reaction conditions due to the inert nature of the MoS_2 surface. To activate the MoS_2 basal plane to improve surface reactivity, we have formed well-controlled densities of defects using Ar^+ sputtering. The defective surfaces were exposed to 1 mbar of H_2O vapor for temperatures ranging from 300 to 600 K. Changes in the APXPS Mo 3*d*, S 2*p*, and O 1*s* core levels indicate that the surface is much more reactive to H_2O, with the formation of Mo-O bonds. These results are consistent with the reduction in the H_2O gas phase which was measured by operando mass spectrometry. We have found that the reactivity strongly depends on the temperature and the size and density of defects. Following this first report of APXPS on MoS_2 acquired at more realistic pressure, we will also report the HER activity and X-ray absorption spectroscopy (XAS) on the pristine surface and compare it with defective surfaces. Our findings demonstrate that the reactivity and the catalytic activity of MoS_2 are significantly improved through the formation of defects.

11:40am **2D+AS+MI+NS-TuM-12 Surface Characterization of 2D Materials and their 3D Analogues using XPS***, **Jonathan Counsell**, S Coultas, C Blomfield, N Gerrard,* Kratos Analytical Limited, UK*; C Moffitt,* Kratos Analytical Limited*; A Roberts,* Kratos Analytical Limited, UK

Since the synthesis of Graphene in 2004 there has been significant interest in novel 2D materials. Indeed this area has produced an abundance of high impact publications and so far >$10bn has been committed globally to both fundamental research and commercialisation. This interest has been due to the unique properties exhibited such as mechanical strength and charge/heat transfer. The potential commercial possibilities are diverse with applications as varied as heat management and dissipation to increasing computer processing power. To fully understand the nature and potential of these materials a comprehensive surface characterisation is necessary.

Herein we illustrate how by applying conventional surface analysis techniques with novel methodologies it is possible to create a more complete picture of the chemical and physical nature of deposited 2D materials. Both organic and inorganic 2D materials will be explored to demonstrate the methods and capabilities. Dichalcogenide materials (sulphides and selenides) containing different metal centres were analysed with XPS, and angular resolved methods, to calculate layer thicknesses, stoichiometry and chemical states. The lateral distribution of CVD ultra-thin films was studied using both macro and micro area XPS imaging modes to distinguish uniformity and evenness. The application of UPS will explore the bonding structure, sensitivity of the materials and as a potential tool for identifying damage/defects in the surface lattice. The merits and pitfalls of ion etching will be discussed and a complete method and protocol will be proposed for limiting spectral artefacts and therefore misleading results. The effects of deposition and analysis on the 2D materials' structure and composition will be highlighted as will the characterisation of unwanted reduction/oxidation, contamination and structural defects. Utilising the complete surface analysis tool box allows the analyst to gain further insight and to fully understand the complex nature of these novel materials.

12:00pm **2D+AS+MI+NS-TuM-13 Characterization of Catalytic Active Sites on the Surface of MoS2 2-D Materials*, Miguel Jose Yacaman,*** University of Texas at San Antonio*; T Zepeda, S Fuentes Moyado,* CNyN UNAM Ensenada, Mexico

Materials such as the MoS2 have been used in catalysis at industrial level for many decades mostly on the hydrodesulfurization of naftas.

However more stringent regulations about the sulfur amount in diesel has printed the need to improve the catalysts .In order to achieve that it is important to understand the nature of the active sites and ways to improve the activity.In this presentation we discuss the use of in-situ techniques to study the surfaces of MoS2 materials made of few layers and discuss the role of the sites on the crystal edges.We also demonstrate that during the reaction the MoS2 material becomes crumpled and changes from semiconductor to metallic.

Actinides and Rare Earths Focus Topic
Room A215 - Session AC+AS+LS-TuM

Chemistry and Physics of the Actinides and Rare Earths

Moderators: Melissa Denecke, University of Manchester, UK, James G. Tobin, University of Wisconsin-Oshkosh

8:00am **AC+AS+LS-TuM-1 Study of the Early Actinide Oxides and Fluorides – Systematics of the Electronic Structure*, Thomas Gouder,*** *R Eloirdi, R Caciuffo,* European Commission - Joint Research Centre, Germany **INVITED**

Oxidation properties of uranium have a great influence on the stability of nuclear waste. U^{VI} has

a 1000 times higher solubility in water than U^{IV}, and so the dissolution of UO_2 based spent fuel nuclear waste strongly depends on the oxidation state of the surface. Oxygen incorporation into the surface of UO_2 first results in the formation of U(V), found in UO_{2+x} and mixed valent oxides, and then formation of U^{VI}. But despite early reports on the existence of a pure U(V) phase (U_2O_5) there are no spectroscopic data on pure U(V). This may be due to its position between the highly stable UO_2 and UO_3. Also, apparent mixed surface phases containing U^{IV}, U^{V} and U^{VI} may result from the strong redox gradient between the oxidizing environment and the reduced bulk, present in most corrosion experiments. Replacing bulk samples by thin films allows avoiding this problem, by confining the reaction to a thin region where final conditions are reached everywhere simultaneously, keeping the system homogeneous. This opened the path for a systematic study of the evolution of the electronic structure of uranium upon oxidation and follow the outer shell configuration from $5f^2$ (U^{IV}), to $5f^1$ (U^{V}) to $5f^0$ (U^{VI}).

We will present electron spectroscopy (XPS, UPS and BIS) and Electron Energy Loss (ELS) study of U_2O_5 compare results to the neighbouring oxides (UO_2 and UO_3). U_2O_5 has been produced by exposing UO_2 successively to atomic oxygen, leading to UO_3, and to atomic hydrogen. Films have been deposited on polycrystalline gold foils (inert substrate). During gas exposure the samples were heated to 400°C to ensure fast diffusion and equilibrium conditions.

Determination of the U oxidation states was based on the characteristic U-4f core level satellites, separated from the main lines by 6, 8 and 10 eV for U^{IV}, U^{V} and U^{VI}, respectively. We managed producing films which showed exclusively a single 8 eV satellite, indicating the presence of pure U^{V}. The formation of U^{V} was confirmed by the intensity evolution of the U*5f* valence emissions. Also the linewidth of the XPS *5f* line decreases from UO_2, with the $5f^1$ final state multiplet, to U_2O_5, with a $5f^0$ final state singlet. The U-5d line also displays a multiplet structure due to interaction with the open 5f shell (U^{IV} and U^{V}). Evolution of the O2p/O1s intensity ratio indicates increasing covalence of the U-O bond in higher oxides.

U oxide spectra will be compared to spectra of ThO_2. Multiplet splitting and its dependence on the open shell was followed by comparing $5f^2$ (UO_2) and $5f^0$(ThO_2) systems. Finally XPS/BIS of the valence region will be presented for various oxides (UO_2, U_2O_5, UO_3 and ThO_2) and fluorides (UF_4 and ThF_4).

8:40am **AC+AS+LS-TuM-3 Broadening of the XPS Spectra of U Oxides*, Paul S. Bagus,*** University of North Texas*; C Nelin,* Consultant **INVITED**

It is common to attempt to improve the energy resolution of XPS in order to obtain more information about the electronic structure. However, it may not be possible to improve the resolution because unresolved final states are present. When the energy separations of these states are less than or comparable to the lifetime of the core-hole, it will not be possible to resolve the states and there will only be a broadening, often quite significant, for the observed peak. The unresolved features may arise from closely spaced multiplets for the angular momentum coupling of the open shell electrons and from excitations to higher lying vibrational levels for the final ionic states; the later is especially important when bond distances for the core-ionized states are very different from those for the initial state; see, for example, Ref. [1] . Thus, for example, the $U(5f_{7/2})$ peak of UO_2 has a FWHM of 1.4 eV although the instrumental resolution was 0.3 eV. [2] Similar large FWHM have been observed for U in different oxidation states. [3-4] In order to be able to relate the widths of these broadened features to the chemical and physical interactions in the system, it is necessary to understand the separate contributions of the multiplet splittings and the vibrational excitations. It has been shown that, for U(IV) 4f XPS in UO_2, the contributions of the multiplet splitting and the vibrational excitations are comparable, each contributing ~0.5 eV to the FWHM. [2] In the present work, the contributions of these mechanisms are examined for U(IV), U(V), and U(VI) oxidation states. In addition, the broadening is examined for the XPS of different core levels where the relative importance of multiplet and vibrational broadening is different from that for the U(4f) XPS. Furthermore, the importance of temperature for the vibrational broadening is also examined. The theoretical predictions for these different parameters can be validated [4] paving the way to extract chemical information from the measured FWHM. [5] The theoretical framework for these predictions is based on wavefunctions for embedded cluster models of the oxides which allows for a balanced treatment of spin-orbit, angular momentum coupling, and covalent bonding.

1. C. J. Nelin et al. Angew. Chem. Int. Ed. 50, 10174 (2011).

2. P. S. Bagus, C. J. Nelin, S. Rennie, G. H. Lander, and R. Springel, (In preparation).

3. T. Gouder, R. Eloirdi, and R. Caciuffo, Scientific Reports 8, 8306 (2018).

4. T. Gouder, R. Eloirdi, R. Caciuffo, and P. S. Bagus, "XPS Broadening in U Oxides", (In preparation).

5. P. S. Bagus, E. S. Ilton, and C. J. Nelin, Catal. Lett. 148, 1785 (2018).

9:20am **AC+AS+LS-TuM-5 Multiscale Characterization of Lanthanide and Actinide Nanoparticles Embedded in Porous Materials*, Stefan Minasian,*** *S Alayoglu, S Aloni,* Lawrence Berkeley National Laboratory*; J Arnold,* University of California at Berkeley*; E Batista,* Los Alamos National Laboratory*; A Braun, C Booth, A Herve,* Lawrence Berkeley National Laboratory*; Y Liu,* University of California at Berkeley*; L Moreau,* Lawrence Berkeley National Laboratory*; T Lohrey, J Long, M Straub, S Robin, D Russo,* University of California at Berkeley*; D Shuh,* Lawrence Berkeley National Laboratory*; J Su, P Yang, X Zhang,* Los Alamos National Laboratory **INVITED**

Decades of synthetic work has shown that desirable physical properties can be obtained by tailoring the size and composition of main-group and transition metal nanoparticles. The origin of these phenomena can be traced to a variety of factors that are intrinsic to nanoparticles, including but not limited to (1) quantization of the electronic states and (2) increasing contributions from nanoparticle surfaces. Despite this progress, very few methods provide the level of synthetic control needed to prepare lanthanide and actinide nanoparticles with well-defined sizes and compositions. Furthermore, many conventional methods of characterization are unable to determine the relative roles of volume and surface chemistry on physical behavior involving the 4f- and 5f-electrons.

We established syntheses for lanthanide and actinide nanoparticles by adapting a conceptual approach employed previously by Fischer and Suh to form d-block transition metal and main-group element nanoparticles in metal organic frameworks (MOFs). Implantation of lanthanide and actinide precursor molecules in covalent organic frameworks (COFs) was achieved by sublimation, followed by decomposition to form nanoparticles via exposure to reactive gases and/or elevated temperatures. A multi-pronged imaging and spectroscopic strategy was developed to fully characterize the complex multi-component materials. The characterization techniques are complementary in that they provide atomic to micron-scale probes, element and bulk-level selectivity, and measurements that are individual and statistically significant (Figure 1). Transmission electron microscopy (TEM) showed that the COF-5 templates limited UO_2 nanoparticle growth to between 1-3 nm, which is similar to the COF-5 pore size (2.7 nm). In addition, small-angle X-ray scattering (SAXS) was used to determine the nanoparticle form factor (for size and polydispersity) in a globally-averaged manner. Scanning transmission X-ray microscopy (STXM) was used to probe micron-scale morphology and to evaluate composition with X-ray absorption spectroscopy at the B, C, and O K-edges. Finally, X-ray absorption fine structure (XAFS) spectroscopy was used to determine composition and structure because it does not require long-range crystallographic order, and because it is capable of probing the nanoparticles selectively despite the substantial background from the organic host. This presentation will also discuss our efforts to show how 4f and 5f-electron behavior changes with variations in size and composition at the nanometer level.

11:00am **AC+AS+LS-TuM-10 Multiple Forms of Uranium Hydrides and their Electronic Properties***, **Ladislav Havela**, V Buturlim, E Chitrova, O Koloskova, P Minarik, M Cieslar, M Dopita, L Horak, M Divis, I Turek,* Charles University, Prague, Czech Republic*; D Legut,* VSB-Technical University of Ostrava, Czech Republic*; T Gouder,* European Commission - Joint Research Centre, Germany

Although the published U-H binary phase diagram contains only the UH_3 phase, a recent progress in sputter deposition synthesis led to the discovery of UH_2, which is with its CaF_2 structure type analogous to e.g. PuH_2 or YH_2 [1]. In addition, a high pressure synthesis yielded several U hyper-hydrides (as UH_8), which are predicted to be a high-temperature supreconductors [2]. As both UH_3 (appearing in two structure modifications, α- and β-UH_3) and UH_2 allow alloying with selected transition metals, we have a whole spectrum of U-H hydrides and certain general features can be deduced, which have a serious implications for our understanding of actinides in general.

The striking fact that both UH_3 phases have, despite very different crystal structure, practically identical size of U moments and magnentic ordering temperature $T_C \approx$ 165 K, which do not change even in the nanostructured state (grain size several nm) is underlined by the fact that both parameters only weakly depend on substantial alloying with Mo and other *d*-metals. UH_2 with substantially larger U-U spacing is a ferromagnet, as well, its $T_C \approx$ 125 K. Structure of all those forms contains identical building blocks, H atoms inside U tetrahedra of invariable size, which are only set up into different patterns. The U-H bonding seems to be therefore an ingredient, which is more important than the conventional U-U spacing. The nature of the bonds is revealed by ab-initio calculations. One general feature is the U-6*d* hybridization with the H-1*s* states, which leads to an electron transfer towards H. However, unlike rare-earth trihydrides, UH_3 remains metallic, UH_2 naturally, too. The 5*f* states largely released from the 5*f*-6*d* hybridization can therefore develop a strong ferromagnetism despite low U-U spacings. The transfer could be traced even in the real space using the Bader analysis.

The ab-initio techniques, which are successful in capturing the equilibrium volumes and U magnetic moments, are so far less successful in description of photoelectron spectra close to the Fermi level, which indicates importance of electron-electron correlations.

This work was supported by the Czech Science Foundation under the grant No. 18-02344S.

[1] L. Havela et al., Inorg. Chem. 57 (2018) 14727.

[2] I.A. Kruglov et al., Sci. Adv. 4 (2018) eaat9776.

11:20am **AC+AS+LS-TuM-11 Hafnium L-Edge X-ray Absorption Near Edge Structure Spectra Reveals Crystal Field Splitting***, **David Shuh**, D Caulder,* Lawrence Berkeley National Laboratory*; L Davis,* Pacific Northwest National Laboratory*; M Mara,* University of California at Berkeley*; C Booth,* Lawrence Berkeley National Laboratory*; J Darab, J Icenhower, D Strachan,* Pacific Northwest National Laboratory

One method for the safe disposal of actinides currently under consideration by the U.S. Department of Energy is immobilization of radionuclides in a glass or ceramic wasteform that will subsequently be stored in a geological repository. To develop successful, stable wasteforms, it is necessary to acquire an understanding of the fundamental chemistry of the actinides (U, Pu, etc.) and neutron absorbers (B, Gd, Hf) that will be incorporated into the glass or ceramic matrix. The X-ray absorption near edge structure (XANES) at the hafnium L_3 and L_1 absorption edges has been investigated to elucidate the local structure of Hf in wasteform glasses that are currently being considered as candidates for the immobilization of radionuclides. During our investigations of the structure of Hf, a neutron absorber and potential Pu(IV) surrogate, we noted an unusual feature at the white line maximum at the L_3 absorption edge: The examination of a variety of Hf model compounds demonstrates that the second derivative of the Hf L_3 XANES displays structure characteristic of crystal field splitting of the empty d-manifold. The peralkaline glasses studied exhibit L_3 XANES spectra typical of Hf in an octahedral crystal field. The L_1 XANES data corroborate these results, as the L_1 spectra of the glasses also resemble that of an octahedral Hf siloxane model compound, distinct from spectra of other standards measured.

11:40am **AC+AS+LS-TuM-12 Electrical Resistivity in Uranium-based Thin Films***, **Evgeniya Tereshina-Chitrova**, L Havela, M Paukov, M Dopita, L Horak, M Cieslar,* Charles University, Prague, Czech Republic*; Z Soban,* Institute of Physics, Academy of Sciences of the Czech Republic, Czech Republic*; T Gouder, F Huber, A Seibert,* Joint Research Center, European Commission, Germany

Metallic 5*f* materials have a very strong coupling of magnetic moments and electrons mediating electrical conduction. It is caused by strong spin-orbit interaction together with involvement of the 5*f* states in metallic bonding. In this work we investigate the electrical resistivity $\rho(T)$ of various uranium-based thin films using the Van der Pauw method. Thin film samples of U-Mo and their hydrides were prepared by reactive sputter deposition [1]. The basic in-situ diagnostics was performed using a photoelectron spectroscopy (XPS). The films were further characterized using x-ray diffraction (XRD) methods and Transmission Electron Microscopy (TEM). The $\rho(T)$ of the films studied correspond to known bulk systems of equivalent composition but provide much more variability of concentrations and geometries.

We studied superconductivity in the U-Mo films by measuring low-temperature resistivity down to 0.4 K. The 100 nm-thick $U_{0.79}Mo_{0.21}$ film shows a transition to the superconducting state at 0.55 K. The transition is wide and extends to 0.4 K. The upper critical field for the thin U-Mo film is ~1 T, i.e. much lower that for the bulk U-Mo obtained by splat cooling [2].

The hydrides of the U-Mo films had to be prepared using a cooled substrate (≈ 177 K). The study of the $(UH_3)_{0.74}Mo_{0.26}$ of estimated thickness 210 nm showed that it is a ferromagnet with the Curie temperature of ≈165 K, i.e. equivalent to bulk UH_3, which underlines the general insensitivity of U hydrides to structure modifications. Overall temperature dependence is very weak and the absolute value of 2 mΩcm, estimated from the nominal thickness, is very high for a metallic system.

The net negative resistivity slope in the U-Mo films and hydrides can be attributed to the randomness on atomic scale, yielding very strong scattering of electrons and weak localization. In the hydrides it is supported also by random anisotropy, randomizing local directions of U moments.

The work is supported by the Czech Science Foundation under the project #18-02344S. Part of the work was supported by “Nano-materials Centre for Advanced Applications,” Project No.CZ.02.1.01/0.0/0.0/15_003/0000485, financed by ERDF.

[1] Gouder, R. Eloirdi, F. Wastin, E. Colineau, J. Rebizant, D. Kolberg, F. Huber, Phys.Rev. B **70**, 235108 (2004).

[2] N.-T. H. Kim-Ngan, S. Sowa, M. Krupska, M. Paukov, I. Tkach and L Havela, Adv. Nat. Sci: Nanosci. Nanotechnol. **6**, 015007 (2015).

Applied Surface Science Division
Room A211 - Session AS+BI+RA-TuM

Quantitative Surface Analysis III/Other Surface Analysis Methods

Moderators: Karen Gaskell, University of Maryland, College Park, Alexander Shard, National Physical Laboratory

8:00am **AS+BI+RA-TuM-1 Oxygen Energy Filtering and Relative Sensitivity Factor Considerations for Making U and Pu Measurements by LG-SIMS***, **Todd Williamson**,* Los Alamos National Laboratory **INVITED**

During nuclear facility inspections, inspectors collect materials intended to show a history of the operations that have taken place within a facility. These materials can be particles obtained using cotton swipes, solid discarded or operationally related nuclear materials, or other items contaminated with nuclear materials. Analysis of these samples is an extremely powerful tool with which to determine facility operations and history. Uranium analysis by SIMS is a mature technique used by the IAEA and its Network of Analytical Laboratories for treaty verification. The analysis of mixed uranium-plutonium particles and solids is not as mature as a capability and has been identified by the IAEA as topic for increased R&D.

This presentation will cover two technical topics related to the analysis of mixed uranium-plutonium materials, relative sensitivity factors (RSF) and energy filtering to improve hydride correction. For a material that contains both U and Pu, while both elements will be sputtered and become ionized during SIMS analysis, they will do so with different efficiencies. This ionization difference tends to be sample-type (matrix) dependent. This phenomenon is known as the relative sensitivity factor (RSF). This presentation will discuss our investigations into determining accurate RSF values for U:Pu and U:Np inter-element measurements. With accurate RSF values, which should be universal for a given sample type, the measured inter-isotope ratios can be corrected to their true values. In a mixed actinide sample, there is ^{239}Pu present which will be unresolvable from ^{238}U^{1}H. This will prevent a conventional hydride correction on measurements, and there are not other clean masses in a mixed actinide sample where a hydride signal can be easily measured. Without a hydride correction the measurement of smaller concentration isotopes will have poor accuracy due to interference from large hydride interferences from major isotopes, and ^{239}Pu measurements will be highly inaccurate. The presentation will discuss our use of energy filtering mediated by an intentionally introduced partial pressure of oxygen in the sample analysis chamber, which changes ionization behavior.

8:40am **AS+BI+RA-TuM-3 Utilizing Large Geometry Secondary Ion Mass Spectrometry for Age-Dating of Individual Uranium Particles***, **Christopher Szakal**, D Simons, J Fassett,* National Institute of Standards and Technology (NIST)*; A Fahey,* Corning Inc.

Secondary ion mass spectrometry (SIMS) is routinely utilized by the International Atomic Energy Agency (IAEA) and its global partner laboratories for the isotopic analysis of individual uranium particles as part of nuclear safeguards efforts. One additional isotopic analysis that has repeatedly been requested by the IAEA involves the development of a capability to perform single particle age-dating, which would provide information about the last time that the nuclear material was purified or enriched. Previously reported efforts in multiple countries have reported the ability to use SIMS and/or large geometry (LG)-SIMS for this purpose, but with the caveat that the measurement can only be viable if the particles are large enough, old enough, and/or enriched enough. We present a new methodology, complete with propagated uncertainties, that advances the individual uranium particle age-dating measurement to include smaller, younger, and lower enriched nuclear material than previously envisioned. Additionally, we will provide insights into utility of this measurement advance within the aims of global nuclear safeguards objectives.

9:00am **AS+BI+RA-TuM-4 Peak Shape Analysis in TOF SIMS: Best Practices and Limiting Precision in Accounting for Detector Saturation***, **Lev Gelb**, A Walker,* University of Texas at Dallas

We compare strategies for analyzing high-mass resolution TOF SIMS data sets affected by detector saturation. 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 ion 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.

We demonstrate an approach to correct for dead time errors in which a probability model for the detector behavior is developed and used in peak fitting of the "uncorrected" data. This approach has many advantages over previous methods which required an estimate of the variance, and it behaves better under conditions of poor data quality (low counts or high saturation.)

Using both synthetic and experimental data, we examine how saturation affects apparent peak shape, position and intensity, the effects of background on estimated peak position and shape, the dependence of peak-location precision on the total number of counts, how interference between satellite peaks is best accounted for, and the biases exhibited by different data analyses. Finally, we extend these methods to imaging data taken at high mass resolution and compare the results obtained with analyses performed at unit-mass resolution.

9:20am **AS+BI+RA-TuM-5 Electronic Structure and Band Gaps of Industrially Relevant Materials Investigated by Photoelectron Spectroscopy and REELS (Reflection Electron Energy Loss Spectroscopy)***, **Paul Mack**, T Nunney,* Thermo Fisher Scientific, UK*; H Meyer III,* Oak Ridge National Laboratory

Many inorganic and organic materials have been created and evaluated for use in a diverse range of applications, such as microelectronics, solar cells and TV displays. The electronic properties of these materials can be tuned by modifying their elemental or chemical state composition. Ideally, the analyst would like to characterize both the composition and electronic properties of a given material in a single experimental run, enabling correlation between electronic properties and composition to be established.

In this work thin films of industrially relevant materials, such as polydioctylfluorene, which is a polymer light emitting diode (PLED), and HfO_2 were analysed using a multi-modal approach. (Thermo Scientific ESCALAB Xi$^+$ and Nexsa tools, configured with multiple surface analysis techniques, were used for the analysis.)

X-ray photoelectron spectroscopy was used to measure elemental and chemical state composition (together with some electronic information) and ultraviolet photoelectron spectroscopy was used to measure ionization potentials and the energies of the highest occupied molecular orbitals (HOMOs). Information about the band gap and lowest unoccupied levels (LUMOs), which cannot be determined with XPS or UPS, was measured with REELS. Energy level diagrams for the materials could then be constructed using the information from the complementary spectroscopic techniques.

Due to the low kinetic energy of photoelectrons generated by the ultraviolet source, UPS is a particularly surface sensitive spectroscopy. When analyzing samples stored in the atmosphere, the resulting data is typically dominated by surface adventitious carbon. This carbon needs to be removed, but with care not to damage the underlying material being studied. The use of an argon cluster ion beam for this kind of careful sample preparation was demonstrated in this work.

9:40am **AS+BI+RA-TuM-6 Practical References for Low Energy Ion Scattering by Ca and F***, S Průsa, T Šikola,* Brno University of Technology, Czech Republic*; **Hidde Brongersma**,* IONTOF Technologies GmbH, Germany/Eindhoven University of Technology, Eindhoven, The Netherlands, Germany

Low-Energy Ion Scattering (LEIS) is known for its extreme surface sensitivity. It is just as well suited for the analysis of amorphous, isolating, extremely rough surfaces, as for flat single crystals. Thus LEIS is applicable to any type of sample that can be taken into vacuum. Since matrix effects are generally absent, or relatively small in LEIS, a quantitative analysis is straightforward. However, the theory to quantitatively predict the atomic sensitivities of the elements falls short. Therefore, an accurate quantification relies on well-defined reference materials. Practical references should be chemically inert, easy to clean and inexpensive. The powder of calcium fluoride, CaF_2, has been suggested as practical reference for Ca and F [1], while the powder of calcium carbonate, $CaCO_3$, has also been suggested for Ca [2].

A complication is that the composition of the outer atomic layer of a material is generally fundamentally and radically different from that of the atoms below this surface. Thus it is unlikely that the F/Ca ratio in the outer surface of CaF_2 will be 2. In fact, precisely this difference makes the LEIS information unique and complementary to that of analytic techniques such as XPS, Auger and (TOF-) SIMS which probe several to many atoms deep. The difference is also highly relevant, since the outer atoms of a surface largely control important processes as adhesion, catalysis, electron emission and growth

It will be shown how the F/Ca atomic ratio, the Ca and F atomic densities, as well as the roughness factors for CaF_2 and $CaCO_3$ have been determined.

[1] T. Gholian Avval, C.V. Cushman, P. Brüner, T. Grehl, H.H. Brongersma, M.R. Linford,

Surf. Sci. Spectra, to be published (2019)

[2] R.M. Almeida, R. Hickey, H. Jain, C.G. Pantano, J. Non-Cryst. Solids 385 (2014) 124

11:00am **AS+BI+RA-TuM-10 Extreme-Ultraviolet-Assisted Atom Probe Tomography***, **Norman Sanford**, L Miaja Avila,* National Institute of Standards and Technology (NIST)*; P Blanchard,* National Institute of Sandards and Technology (NIST)*; D Diercks, B Gorman,* Colorado School of Mines*; A Chiaramonti,* National Institute of Sandards and Technology (NIST)

Laser-assisted atom probe tomography (L-APT) often returns compositional biases that deviate from a specimen's true chemical makeup [1]. In our L-APT studies of GaN, which utilize a 355 nm laser, we find stoichiometric composition (50% Ga, 50% N) only when the pulse fluence is roughly 2E-7 J/cm^2. Higher fluences return nonphysical, Ga-rich compositions; lower fluences give nonphysical N-rich compositions. L-APT of other materials, including SiO2, exhibit similar biases. L-APT is a thermally-activated mechanism. The specimen is subjected to a strong electric field that is held just below the threshold for field evaporation of ions; evaporation is triggered by thermal transients imparted by the incident laser pulses.

Motivated by the need to improve the quantitative accuracy of atom probe tomography, we explored an alternative, photoionization-triggered pathway for field evaporation by replacing the conventional laser on an L-APT tool with a pulsed, extreme-ultraviolet (EUV) source—thus realizing the XAPT [2,3]. The tabletop EUV source is an ultrafast, amplified Ti:sapphire laser driving an Ar-filled capillary waveguide. Pulsed, coherent EUV is produced via high-harmonic generation [4]. The respective characteristics of EUV pulse width, repetition rate, wavelength (energy), and fluence, incident on a specimen tip are: 10 fs, 10 kHz, 30 nm (42 eV), and 2.5E-8 J/cm^2. Comparative XAPT and L-APT analyses were performed on specimens of GaN and SiO2 (amorphous fused silica). For SiO2, L-APT returned an off-stoichiometry composition of 41% Si and 59% O; XAPT yielded 33% Si and 66% O (stoichiometry). For GaN, XAPT found 49% Ga and 51% N; L-APT yielded laser-pulse-fluence-dependent composition and returned 68% Ga and 32% N for a fluence of roughly 2E-6 J/cm^2; L-APT conditions giving stoichiometric GaN appear above. The uncertainty of these measurements is 1—3 at. %. All specimens were examined at 50 K. XAPT-derived mass spectra show reduced occurrences of molecular ions and reduced "thermal tails" (persistent field emission following the laser pulse). Ongoing work for presentation at the meeting includes comparative studies of InGaN, Mg:GaN, and AlGaN. In all cases examined thus far, the XAPT approach offers measurable improvements over L-APT.

1. D. J. Larson, et al, Local Electrode Atom Probe Tomography (Springer, New York, 2013)
2. A. N. Chiarmonti, et al, MRS Advances (in press, 2019)
3. L. Miaja Avila, et al, Frontiers in Optic (FiO), Optical Society of America, Wash. DC, p. FTu5C. 3 (2018)
4. L. Miaja Avila, et al, Phys. Rev. Lett. 97, 113604 (2006)

11:20am **AS+BI+RA-TuM-11 A Multi-Technique Approach for Complete Thin Film Characterisation***, **Sarah Coultas**, J Counsell, N Gerrard, C Blomfield,* Kratos Analytical Limited, UK*; C Moffitt,* Kratos Analytical Limited*; T Conard,* IMEC, Belgium

The application of thin film technology is of commercial importance across a range of industries and is commonly used to influence both the physical and chemical properties of bulk materials. Ranging in thickness from tens of Angstroms to microns, their applications are used across a broad range of disciplines including the semiconductor, biomaterial and energy harvesting industries. Herein, we provide a multi-technique investigation of layered thin film and ultra-thin film coatings using a model system for gate oxide structures. The combination of techniques allows one to build a complete picture of the chemistry of these materials and how subtle differences in chemistry and stoichiometry can influence the properties of a substrate to enhance its application specificity.

X-ray Photoelectron Spectroscopy (XPS) was used to characterize the surface chemistry of these layered thin film materials. Using monochromated Al-Kα (1486.6 eV) X-rays, it was possible to gain quantitative chemical information from the uppermost 10 nm of the surface. In this study, we illustrate how angle-resolved XPS (ARXPS) can be used as a more surface sensitive approach to probe only the topmost 1-3 nm, and how one can utilize maximum entropy modelling (MEMS) to recreate a concentration depth profile from the resulting data.

In contrast to increased surface sensitivity, high energy excitation sources can be used to extend the analysis depth of a material to >15 nm. Here, we describe the use of a monochromated Ag-Lα (2984.2 eV) X-rays to delve deeper into the bulk structure. In combination with ARXPS, the greater excitation energy and increased analysis depth allows one to measure elemental core levels which are not accessible using the conventional Al-Kα source. In light of this, one can build a more detailed description of the structure of these thin film materials and their use in relevant applications.

11:40am **AS+BI+RA-TuM-12 Polymeric Barrier Coatings for Silicone Elastomer against Diffusion of Isocyanate in Vacuum Casting Processes***, **Martin Wortmann**, R Petkau,* Bielefeld University of Applied Sciences, Germany*; N Frese,* Bielefeld University, Germany*; E Moritzer,* Paderborn University, Germany*; A Gölzhäuser,* Bielefeld University, Germany*; B Hüsgen,* Bielefeld University of Applied Sciences, Germany

The vacuum casting process is used industrially to replicate prototypes of polyurethane (PUR). Due to the diffusion of 4,4'-methylene diphenyl diisocyanate (MDI), a PUR resin component, the silicone casting molds used in this process show a progressive degradation, which leads to the failure of the casting molds after a few casting cycles [1]. In this contribution, we present ways to protect the surface of the silicone elastomer by various thermoplastic polymer coatings. The polymers investigated were dissolved in different volatile solvents and coated on pretreated silicone surfaces. For this purpose, the compatibility of those polymer solutions with polydimethylsiloxane (PDMS) was investigated and their diffusion coefficients with respect to MDI were measured. Polymer coatings that have exhibited a high diffusion barrier have been used to drastically increase the output of the casting molds.

[1] M. Wortmann et al., *Polymer Plast Tech Eng* 57, 1524 (2018).

12:00pm **AS+BI+RA-TuM-13 pARXPS Study of GeSbTe Surface Oxidation***, **Ludovic Goffart**,* ST Microelectronics/LTM/CEA-LETI, France*; C Vallée,* Laboratoire des Technologies de la Microélectronique (LTM), France*; B Pelissier,* LTM, Univ. Grenoble Alpes, CEA-LETI, France*; J Reynard, D Benoit,* ST Microelectronics, France*; G Navarro,* CEA-LETI, France

This work is focusing on the oxidation of the well-known GST material ($Ge_2Sb_2Te_5$, GST225) widely used in storage optics like CD, DVD and Blu-ray. This time, we use the GST for its electrical properties to create a non-volatile memory. The GST we use in this work is modified from the GST225 chemical composition to comply with the specifications needed in automotive applications, the most important being a good stability and cycling at high temperature environment.

This non stoichiometric GST composition leads to instability in its structure, therefore more aging and oxidation which conflict with the objectives of this new PCM cell. Added to this is some atomic segregation during crystallographic relaxation, which leads to low cycling durability of the cell and lower crystallization temperatures. To counter these effects, the GST material is doped but this makes more complex the chemical characterization of the material.

To understand and overcome these problems, different GST materials (from 225 to Ge rich) have been characterized using the pARXPS technique which is an angular resolved XPS. With this technique a very complete chemical characterization of the surface of these samples have been performed to gather useful information of atomic segregations and surface oxidation, by acquiring 8 simultaneous angles at the same time for different element windows. This is only possible by developing a complex fitting model for the large amount of spectra obtained. This model has to deal with the complex feature of the spectra obtained since some peaks were overlapping. Physical constraints are then necessary to obtain a realistic fit of the spectra. Once the model optimized, the aging of the samples have been studied by monitoring the evolution of specific XPS shapes with time. As a result, the oxidation kinetic and the thickness of the oxidized surfaces are quantified and finally a depth profile reconstruction of the different chemical bonds is performed. In addition to pARXPS, TEM-EDX analysis were performed to confirm the fitting model developed and profile depth reconstruction obtained with pARXPS technique.

Biomaterial Interfaces Division
Room A120-121 - Session BI+AS-TuM

Characterization of Biological and Biomaterial Surfaces

Moderators: Karyn Jarvis, Swinburne University of Technology, Sally McArthur, Swinburne University of Technology, Australia

8:00am **BI+AS-TuM-1 Characterizing Protein Fiber Structures in Solution with Vibrational Sum-Frequency Scattering Spectroscopy***, **David G. Castner**, P Johansson,* University of Washington

Sum frequency generation vibrational spectroscopy has been developed as a powerful technique for investigating the structure of proteins at flat liquid-solution interfaces. However, many biological processes are regulated by interactions at the interface of 3D structures. Collagen forms large fibers that are responsible for the structural integrity of tissues. The structure, organization and interactions of these fibers are important for the survival, communication, migration, and proliferation of cells. Investigating protein fiber interactions is challenging, particularly under biological conditions. However, vibrational sum-frequency scattering (SFS) spectroscopy, with inherent contrast for local molecular ordering, can be utilized towards these important goals. We have applied SFS to collagen type I fiber networks self-assembled in aqueous environments. Signals were detected from the amide I band stretching vibrations (associated with the protein backbone structure) and signals from the C-H stretching and bending vibrations (associated with the protein side-chains). 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. For randomly oriented fiber networks the amide I chiral signals are dominant in the phase-matched direction. In contrast, amide I achiral and chiral signal strengths are comparable at scattering angles above 6°. The backbone signal intensity decreases significantly as the scattering angle increases. In contrast, the side-chain signals remain high at large scattering angles. Distinctions in the organizational symmetry and the relative fiber surface contribution to the overall signal are probable reasons for these observations. The amide I band the spectra acquired at a scattering angle of 22 degrees provided good specificity to the surface region of the collagen fibers. This surface sensitivity was used to investigate how a dilute sodium dodecyl sulfate surfactant solution affects the spectra and scattering patterns of the SFS signals. The amide I SFS polarization ratios at a scattering angle of 22° provided insights to early changes to the collagen fiber structure. This shows the promise of SFS as an important technique for providing detailed information about the surface structure and chemistry of protein fibers, complementary to what can be obtained from other techniques such as SHG imaging or IR spectroscopy. Thus, SFS can provide a molecular level understanding of the changes to collagenous tissues during decellularization and help optimize the protocols for tissue engineered organs.

8:20am **BI+AS-TuM-2 Near-Ambient Pressure XPS Surface Characterisation of Bacteria and Biofilms - Model Systems and Sample Preparation***, **Marit Kjaervik**,* Bundesanstalt für Materialforschung und -prüfung, Germany*; P Dietrich, A Thissen,* SPECS Surface Nano Analysis GmbH, Germany*; K Schwibbert, W Unger,* Bundesanstalt für Materialforschung und -prüfung, Germany

Bacterial samples are typically freeze dried or cryo-prepared prior to XPS analysis to allow for measurements in ultra-high vacuum (UHV). The sample environment in the near-ambient pressure (NAP) XPS instrument EnviroESCA allows for measurements in up to 15 mbar water vapor, thus, sample preparation is no longer restricted to UHV-compatible techniques.[1] For instance, biofilms grown in medium can be transferred directly from the medium to the measurements chamber, maintaining a humid environment throughout the measurements.[2] Considering the complexity of bacterial samples, sample preparation must be carefully considered in order to obtain meaningful and reproducible results.

In this talk, various strategies for sample preparation of bacteria and biofilms for NAP-XPS measurements will be discussed. Model systems of planktonic bacteria, artificial biofilms resembling the exopolysaccharide matrix and biofilms have been characterised in various conditions. The stability and homogeneity of the samples were assessed by monitoring the C1s core-level peak at different sample locations. The quality of the XP spectra is also influenced by the gas environment, which will be exemplified by core level spectra of *P. Fluorescens* acquired in air, water vapor and ultra-high vacuum.

Furthermore initial results from iodine doped model biofilms will be presented. The in-depth chemcial compositon profile of these model films was obtained using an argon gas cluster ion gun.

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.

[1] P. M. Dietrich, S. Bahr, T. Yamamoto, M. Meyer, and A. Thissen, "Chemical surface analysis on materials and devices under functional conditions – Environmental photoelectron spectroscopy as non-destructive tool for routine characterization," *J. Electron Spectros. Relat. Phenomena*, vol. 231, pp. 118–126, Feb. 2019.

[2] M. Kjaervik, K. Schwibbert, P. Dietrich, A. Thissen, and W. E. S. Unger, "Surface characterisation of *Escherichia coli* under various conditions by near-ambient pressure XPS," *Surf. Interface Anal.*, vol. 50, no. 11, pp. 996–1000, Nov. 2018.

8:40am **BI+AS-TuM-3 ToF-SIMS Imaging of Plant seed Interactions with Plant-growth Promoting Bacteria***, **Yuchen Zhang**, X Yu,* Pacific Northwest National Laboratory

Presentation Summary:

This presentation aims to show that we have successfully used delayed image extraction in time-of-flight secondary ion mass spectrometry (ToF-SIMS) to study the interaction between Brachypodium seed and plant growth-promoting bacteria (PGPB) for the first time.

Abstract

The use of time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a relatively unexplored in plant biology that is undergoing fast development [1]. The majority of existing research in plant biology that has utilized ToF-SIMS mostly involves the study of plant stems and leaves, and only a handful of studies apply it on the analysis of plant roots and/or seeds. Additionally, the use of Brachypodium distachyon (Brachypodium) as a model system for research has become more prominent in plant biology. Brachypodium, a C3 model, can provide more insight into the biological studies of other species including small grain crops such as wheat and barley [2], therefore it has a significant scientific impact in plant biology. To the best of our knowledge, this will be the first systematic ToF-SIMS imaging of Brachypodium. In this work, we obtained chemical mapping of the interaction of grains of Brachypodium with plant growth-promoting bacteria (PGPB) [3], namely, Pseudomonas and Arthrobacter, using ToF-SIMS. Specifically, the use of the delayed image extraction mode in ToF-SIMS provides chemical speciation of the Brachypodium seed surface and simultaneously captures the morphological features of the plant-bacteria interface. Our findings provide high resolution spatial distributions of fatty acids (e.g., palmitic acid, stearic acid, and arachidic acid) and phospholipid (e.g., cardiolipin) present on the Brachypodium seed surface. Spectral PCA results indicate that the biofilm and planktonic cells both have effects on the seed surfaces. In terms of seedling potentials, the seed brush is the most active after PGPB attachment on the biointerface.

Key words: ToF-SIMS, delayed image extraction, PGPB, Brachypodium, Pseudomonas, Arthrobacter

References:

1. Boughton, B.A., et al., Mass spectrometry imaging for plant biology: a review. Phytochem Rev, 2016. 15: p. 445-488.

2. Delaplace, P., et al., Influence of rhizobacterial volatiles on the root system architecture and the production and allocation of biomass in the model grass Brachypodium distachyon (L.) P. Beauv. BMC Plant Biol, 2015. 15: p. 195.

3. Scholthof, K.B.G., et al., Brachypodium: A Monocot Grass Model Genus for Plant Biology. Plant Cell, 2018. 30(8): p. 1673-1694.

9:00am **BI+AS-TuM-4 Visualization of Signaling Molecules in Brain Tissue by Multimodal Imaging with Matrix Assisted Laser Desorption/Ionization Mass Spectrometry and Time-of-Flight Secondary Ion Mass Spectrometry***, **Matthias Lorenz**, S King, N Borodinov, C Steed, J Chae, A Ievlev, O Ovchinnikova,* Oak Ridge National Laboratory

Matrix Assisted Laser Desorption/Ionization (MALDI) is commonly used for the chemical imaging of biological tissue samples with mass spectrometry due to its capability to desorb and ionize large organic molecules with limited fragmentation, thus preserving a high degree of molecular information. MALDI is suitable to analyze species such as peptides and proteins, and the intact molecular ion is observable in many cases.[1] The achievable spatial resolution using MALDI mass spectrometry imaging (MSI) is limited to about 30 µm using standard matrix compounds, primarily due to the dimensions of matrix crystals and the stability of the matrix coating.[2] Time-of-Flight (ToF) Secondary Ion Mass Spectrometry (SIMS) is another mass spectrometry based chemical imaging technique that can achieve a spatial resolution below 100 nm.[3] The chemical information obtained from ToF-SIMS analyses is, however, limited to smaller organic molecules and elemental species due to a more significant fragmentation of intramolecular bonds and decreasing ion yields with increasing molecular weight. We present here a workflow comprising the consecutive application of ToF-SIMS and MALDI-ToF-MS MSI to combine the strength of both chemical imaging techniques. Even though mass spectrometry based surface analysis techniques are inherently destructive in nature, the volumes of sample material that the two imaging techniques extract at each sampling location differs significantly (~30 µm vs. ~100 nm craters). This difference enables the assumption of a non-destructive nature for the ToF-SIMS imaging cycle relative to the MALDI sampling volume and spatial resolution, leaving a virtually pristine sample surface for a subsequent MALDI imaging cycle of the same sample area. We showcase the application of our workflow for the multimodal imaging of a coronal mouse brain tissue section, with automated co-registration of the two imaging data sets. We demonstrate how the MALDI mass spectral data enable to complement the high spatial resolution ToF-SIMS MSI data set with an additional degree of molecular structural information and discuss our workflow based on the visualization of signaling molecules in the mouse brain tissue.

[1] Todd, P.J.; Schaaff, T.G.; Chaurand, P.; Caprioli, R.M. *J. Mass Spectrom.* **2001**, *36*, 355−369.

[2] Yang, J.; Norris, J.L.; Caprioli, R. *J. Mass Spectrom*. **2018**, *53*, 1005−1012.

[3] Kollmer, F.; Paul, W.; Krehl, M.; Niehuis, E. *Surf. Interface Anal.* **2013**, *45*, 312–314.

9:20am **BI+AS-TuM-5 *In situ* Observation of Triacylglycerol (C39:0) and Acylceramide (C17) Colocalization in Lipid Droplets of Apoptotic Cells using ToF-SIMS**, ***Shohini Sen-Britain***, *N Li, G Atilla-Gokcumen, J Gardella Jr.,* State University of New York, Buffalo

The formation of phase segregated lipid droplets storing triacylglycerol containing polyunsaturated fatty acyl chains (PUFA-TAGs) during apoptosis, or programmed cell death, has been previously observed [1,2]. Polyunsaturated fatty acids are incorporated into PUFA-TAGs by diacylglycerol acyltransferases (DGATs) [1]. The acylation of ceramide by DGATs also produces acylceramide which has been found in lipid droplets as well [3]. The accumulation of ceramide and PUFA phospholipids sensitizes cells to cell death. Therefore, acylation of these molecules into phase segregated droplets is thought to have a protective effect [1,2].

Previous studies observing these acylated molecules in lipid droplets have utilized LC-MS of fractionated lipid droplets [1-3]. However, colocalization of these lipids has not been observed *in situ*. Previous imaging studies have been limited by the use of nonspecific lipid dyes, such as nile red, in observing lipid droplets.

In this study, we have utilized metal-assisted time-of-flight secondary ion mass spectrometry (ToF-SIMS) to image the colocalization of TAG (C39:0) and acylceramide (C17) in apoptotic HCT-116 human colorectal carcinoma cells. We maintained sample preparation conditions used in previous microscopy studies by cutting out squares of cell culture plates containing lyophilized apoptotic HCT-116 cells. Imaging of lipids within the cells was accomplished by milling off the top half of the cells using a focused ion beam-scanning electron microscope (FIB-SEM). Imaging of gold sputter coated samples in negative ion mode allowed for the observation of high molecular weight secondary ions (>1000 m/z) and of unique spectra of both TAG (C39:0) and AC (C17). Colocalization of endogeneous TAG and AC were observed in apoptotic cells. TAG and AC fragmentations were determined by analyzing (1) gold sputter coated TAG and AC standards on cell culture plates and (2) standard additions of TAG and AC onto milled lyophilized apoptotic cells that were also gold sputter coated.

The work accomplished in this study illustrates the potential of identifying the spatial localization of large biomolecules in cells on insulating, high topography containing samples through the use of standard additions and high mass resolution, metal-assisted ToF-SIMS. The results are also the first reported *in situ* observation of TAG and AC colocalization in apoptotic cells.

[1] *Biochemistry* 2018, 57, 72-80

[2] *ACS Chemical Biology* 2016, 11, 2583-2587

[3] *Cell Metabolism* 2017, 25, 686–697

9:40am **BI+AS-TuM-6 Customizing Decellularized Biopolymer Matrices to Serve as Cell-instructive Microenvironments: A ToF-SIMS Study**, ***Mirko Nitschke***, *V Magno, R Zimmermann, N Dennison,* Leibniz Institute of Polymer Research Dresden, Germany*; C Werner,* Leibniz Institute of Polymer Research Dresden, Germany, Deutschland, Germany

Decellularized extracellular matrix (ECM) preparations provide highly valuable options for the *in vitro* reconstitution of tissue-specific niches. In this approach, control over the ECM composition and structural assembly can be achieved through the modulation of cell culture conditions. We have previously demonstrated that adding ascorbic acid and using macromolecular crowding (MMC) allows for tuning the ECM deposition by human mesenchymal stem cells by boosting procollagen synthesis and enhanced complexation/deposition of soluble matrix components [Prewitz *et al. Biomaterials* **73** (2015) 60]. Combining both options, we have now explored the fabrication of a large set of cell-derived ECM variants which were analyzed by time-of-flight secondary ion mass spectrometry (ToF-SIMS) and immunostaining. Principle component analysis (PCA) of the ToF-SIMS spectra and quantitative immunofluorescence data revealed distinct differences and trends in the complex ECM composition. The introduced methodology is validated by cell culture experiments using the decellularized matrix variants and concluded to provide a new level of control in tailoring matrix properties for tissue and organoid models (authors MN and VM contributed equally).

11:00am **BI+AS-TuM-10 Hierarchical Changes in Protein Structure: from Surface Influence to Cell Control**, ***Sapun Parekh,*** University of Texas at Austin **INVITED**

Protein structure, not just identity, is now appreciated as a critical variable that determines downstream biochemical reactivity. In biomaterials research, proteins are often coated onto materials to make them biocompatible; however, the structure of particular proteins on the material surface is often unknown or not taken into account, leading to inconsistent biological responses. The same protein on different biomaterial surfaces can take on distinct structures that can, for example, lead to differential receptor activation or stem cell differentiation into specific lineages. In this work, we demonstrate how both chemical and physical stimuli modulate protein structure and ultimately direct cell response. In the first part of this talk, I will show how graphene materials, with their unique physico-chemical properties and potential applications in tissue engineering, can strongly modulate fibronectin structure, cellular integrin binding, and stem cell differentiation. In the second part, I will show how physical forces on protein-based fibrin hydrogels can modulate protein structure, modifying enzymatic and integrin binding sites and drastically reducing platelet adhesion. The work presented here shows that physical and chemical properties of materials strongly influence protein structure and downstream biological responses, showing that biomaterial design should include considerations to control protein structure in addition to protein capture.

11:40am **BI+AS-TuM-12 The Role of Cr-N phases Prepared by Plasma Processes on 316L Stainless Steel and the Potential Use in Biocompatible Systems**, ***Diana Galeano-Osorio***, *S Vargas-Giraldo, C Castano,* Virginia Commonwealth University

The corrosion performance of chromium nitride (CrN) phases obtained by two different plasma-based techniques on 316L stainless steel was investigated by electrochemical testing in simulated body fluid, SBF. One method consisted of the surface treatment of 316L stainless steel by plasma nitriding. The other approach comprised the deposition of Cr-N thin film layers on 316L stainless steel substrates by reactive sputtering technique. The structural analysis of the Cr-N phases on the plasma nitrided samples by X-ray diffraction (XRD) showed an expanded austenite phase (S-Phase), while X-ray photoelectron spectroscopy (XPS) analysis revealed the presence of both the S-Phase and CrN. In the case of thin films, the XRD and XPS characterization predominantly showed a CrN phase. The different topographical characteristics of both approaches coupled with the surface energy characteristics and the electrochemical behavior in SBF provided valuable information for the potential use of these materials in biocompatible applications.

12:00pm **BI+AS-TuM-13 Direct Interspecies Electron Transfer (DIET) in Syntrophic Microbes**, ***Cuiyun Yang***, *X Yu,* Pacific Northwest National Laboratory

Presentation Summary:

This presentation will show our recent results of metabolic performance of direct interspecies electron transfer between syntrophic *Geobacter* species by using *in situ* liquid time-of-flight secondary ion mass spectrometry (ToF-SIMS).

Abstract

Direct interspecies electron transfer (DIET) is deemed important and effective for electron exchange among syntrophic Geobacter species. DIET facilitates coupling of carbon, nitrogen, phosphorus biogeochemical cycles in the natural anaerobic environment [1]. In this presentation, Geobacter sulfurreducens and Geobacter metallireducens were employed to investigate the metabolic behavior of a syntrophic community cultured in a SALVI microfluidic reactor and analyzed by *in situ* liquid time-of-flight secondary ion mass spectrometry (ToF-SIMS). More types of molecules that facilitate metallic-like electron conductivity pilis or cellular outer-membrane cytochrome (e.g., OmcS) formation in the *Geobacter* co-culture community were observed than the planktonic cells. Characteristic peaks observed include aromatic acids m/z^+ 82 ($C_4H_6N_2^+$, histidine), 120 ($C_8H_{10}N^+$, phenylalanine), and 166 ($C_9H_{12}NO_2^+$, phenylalanine), benzene polymers m/z^- 93 ($C_6H_5O^-$), 94 ($C_6H_6O^-$), and 133 ($C_9H_9O^-$) in the co-cultured aggregate. The compositions of specific fatty acid also changed according to the culture condition when comparing the single population vs. co-cultured community. Abundance of water clusters were observed in this work and the water cluster differences observed among the cultured community, single population biofilms, or planktonic cells also suggest that other living activities of cells is possible, for instance, moderation of the solvation spheres when forming the aggregates due to IET and/or DIET. Alternatively, we hypothesize that proton-coupled electron transfer (PCET) may play a role in the syntrophic community besides DIET based on *in vivo* spectral comparisons. Our *in situ* molecular imaging results lead to the following conclusions: 1) interspecies electron transfer in co-cultured planktonic states may be mainly mediated by reduced molecular hydrogen; and 2) DIET in co-cultured aggregates functions via direct contact or microbial nanowire. Our findings improve the understanding of the electron transfer in syntrophic communities based on *in vivo* molecular imaging.

Key words: direct interspecies electron transfer (DIET), interspecies electron transfer*, Geobacter sulfurreducens*, *Geobacter metallireducens*, *in situ* liquid TOF-SIMS

References:

1. D.R. Lovley, et al., *Geobacter*: the microbe electric's physiology, ecology, and practical applications. Adv. Microbiol. Physiol., 59, 1-100, 2011.

Actinides and Rare Earths Focus Topic
Room A215 - Session AC+AS+LS-TuA

Forensics, Science and Processing for Nuclear Energy

Moderators: Paul S. Bagus, University of North Texas, Tomasz Durakiewicz, National Science Foundation, David Geeson, AWE

2:20pm **AC+AS+LS-TuA-1 Helium Implantation Studies in Metals and Ceramics for Nuclear Energy Applications, Microstructure and Properties***, **Peter Hosemann**, M Balooch, S Stevenson, A Scott,* University of California, Berkeley*; Y Yang,* Lawrence Berkeley Lab, University of California, Berkeley **INVITED**

Helium damage in materials is a concern for fission and fusion materials. The development of Helium bubbles in a solid can lead to fundamental property changes ranging from embrittlement to surface blistering. Especially shallow ion beam implantation is of interest to the fusion community since the surface degradation of materials is one of the main materials degradation mechanism. This work features a rapid Helium implantation and screening method based on nanometer precise helium implantation using the helium ion beam microscope (HIM). This tool allows multiple doses in the same grain with subsequent rapid materials examination. We evaluate single and polycrystalline SiC, W, Cu, and Ti in this work and find interesting channelling phenomena which have been fit to modelling results from the literature. Further we evaluate mechanical and microstructural property changes using TEM, nanoindentation, AFM and micropillar compression testing on these alloys.

3:00pm **AC+AS+LS-TuA-3 Origin of Element Selectivity during Solvent Extraction of Rare Earths: Studies of Model Interfaces using Synchrotron Radiation***, M Miller, Y Liang, H Li, M Chu, S Yoo,* Northwestern University*; W Bu,* University of Chicago*; M Olvera de la Cruz, **Pulak Dutta**,* Northwestern University **INVITED**

Solvent extraction, commonly used to remove lathanides from aqueous solutions, is known to preferentially extract heavier lanthanides. To understand the underlying nanoscale mechanisms, we studied a model system: extractant monolayers floating on an aqueous solution containing lanthanide ions. X-ray fluorescence near Total Reflection (XFNTR) was used to detect interfacial cations, using synchrotron radiation at the ChemMatCARS facility, Advanced Photon Source.

We found that the interfacial density of adsorbed cations increases very sharply as the solution concentration is increased, reminiscent of a first-order phase transition. The threshold concentration is an order of magnitude lower for erbium (Z=68) compared to neodymium (Z=68). When the solution contains both ions equally, only erbium is found at the extractant interface, and the bulk erbium concentration must be decreased by one order of magnitude relative to neodymium before both species appear equally at the interface.

These results indicate that element selectivity during liquid-liquid extraction occurs at the extractant-laden interface. Electrostatic effects arising from the dielectric mismatch, ionic correlations, and the sizes of the cations can be used to theoretically model the observed behaviors.

4:20pm **AC+AS+LS-TuA-7 Analysis of Aged of Uranium Particles via X-ray Xpectromicroscopy***, **Andrew Duffin**, J Ward,* Pacific Northwest National Laboratory **INVITED**

Uranyl fluoride (UO_2F_2) particles are a common by-product when uranium hexafluoride (UF_6), a volatile form of uranium used in industry, is released into air. Uranyl fluoride particles continue to react in the environment, eventually moving towards uranium oxide. Understanding the chemical changes uranyl fluoride takes is important as the chemical state affects how this contaminant is transported in the environment. We employed scanning transmission X-ray microscopy (STXM) to map the chemical changes that occur in single particles of uranyl fluoride, aged under controlled conditions. We have shown that ligand K-edge X-ray absorption spectroscopy can fingerprint uranium chemical species at the nm spatial scale and we have used this specificity to gain insight into the transformation of uranyl fluoride to uranium oxide.

5:00pm **AC+AS+LS-TuA-9 Heat Transfer and Phase Stability of Early Actinides and Actinide Compounds***, **Dominik Legut**, L Kývala, U Wdowik, G Jaglo, P Piekarz,* Technical University of Ostrava, Ostrava, Czechia*; L Havela,* Charles University, Prague, Czechia **INVITED**

Actinides and especially their carbides as prospective nuclear fuel materials for the generation IV reactors were investigated using the density functional theory. We demonstrate that their electronic, magnetic, elastic, and thermal properties can be at present well described if the spin-orbit interaction and partial delocalization 5f electrons is properly included in the computational approaches. One can well reproduce not only basic electronic structure but also elastic constants, phonon dispersions, and their density of states, provided by XPS, UPS, BIS, and inelastic neutron scattering data [1-4]. The localization of the 5f electrons could be captured using a moderate value of the on-site Coulomb interaction parameter. The case studies include a realistic description of the ground-state properties of elemental metals as Th, U and their monocarbides ThC and UC. The realistic description of the electronic structure and lattice dynamics (phonons) explains much higher thermal expansion and heat capacity in pure actinides (as Th) comparing with respective actinide monocarbides. The modelling also gives an insight up to which temperature the heat transport depends on lattice vibrations and where the electron transport starts to dominate. We can identify the vibration modes influencing the heat transport most. Carbides are compared with actinide oxides, where the major role is played by optical phonon branches [3]. The phase stability and elastic properties have been explored in a cascade of uranium hydrides [5], for which the requirement to reproduce the ferromagnetic moments gives an important feedback for the choice of on-site Coulomb U and Hund's exchange J.

1. U. D. Wdowik, P. Piekarz, D. Legut, and G. Jaglo, Phys. Rev. B 94, 054303 (2016).

2. L. Kyvala and D. Legut (submitted to PRB April 2019)

3. P. Maldonado, L. Paolasini, P. M. Oppeneer, T. R. Forrest, A. Prodi, N. Magnani, A. Bosak, G. H. Lander, and R. Caciuffo, Phys. Rev. B 93, 144301 (2016).

4. Y. Yun, D. Legut and P. M. Oppeneer, J. Nucl. Mat. 426, 109 (2012).

5. L. Havela, M. Paukov, M. Dopita, L. Horak, D. Drozdenko, M. Divis, I. Turek, D. Legut, L. Kyvala, T. Gouder, A. Seibert, F. Huber, Inorg. Chem. 57, 14727 (2018).

5:40pm **AC+AS+LS-TuA-11 Reactivity of Potential TRISO Fuel Barrier Layers (SiC and ZrN) with H_2O Probed with Ambient Pressure Photoelectron Spectroscopy***, **Jeff Terry**, M Warren,* Illinois Institute of Technology*; R Addou, G Herman,* Oregon State University

While the use of TRISO fuels has been long postulated within High Temperature Gas Reactors, another potential use for the TRISO fuels is as an accident tolerant fuel in Light Water Reactors (LWRs). Before TRISO fuels can be used in LWRs, the corrosion properties of the different layers of TRISO fuels must be well understood. Photoelectron Spectroscopy (PES) has long been utilized to study the oxidation behavior of materials due to its sensitivity to both element and chemical state. The problem with PES has been that it has historically been a technique that required Ultrahigh Vacuum conditions for measurements. This made it difficult to study corrosion in situ. New instruments have expanded the capabilities of PES. It is now possible to measure photoemission spectra at ambient pressure. We have measured the in situ corrosion of a SiC layer grown as a TRISO simulant at a pressure of 1 mbar of H_2O at temperatures up to 500 C using an ambient pressure photoemission system. We see no oxidation of the SiC layer by water at temperatures up to 350 C. Above 350 C, the SiC begins to oxidize with the formation of SiO_2. In contrast, ZrN reacts at a pressure of 1 mbar of H_2O at room temperature. As the temperature increases, the ZrN layer is completely converted to ZrO_2. In the TRISO fuel, the barrier layer is surrounded by pyrolytic carbon. We model the protective ability of the outer carbon layer by making multilayers SiC/C and ZrN/C and measuring these under the same conditions. We find that a 2 nm carbon layer prevents the underlying barrier layers from reacting with water.

Applied Surface Science Division
Room A211 - Session AS+BI+CA+LS-TuA

Beyond Traditional Surface Analysis

Moderators: Michaeleen Pacholski, The Dow Chemical Company, Xiao-Ying Yu, Pacific Northwest National Laboratory

2:20pm **AS+BI+CA+LS-TuA-1 Nanotechnology as a Driver for Going Beyond Traditional Surface Analysis***, **Olivier Renault**,* CEA-LETI, France **INVITED**

In the last 10 years, the progress of analytical methods has been more and more strongly connected to the pressing needs from materials and processing developments in the nanoelectronics industry. The field of materials analysis is now expanding as more and more complementary information are needed to tailor new materials for particular applications. Time-consuming techniques in the past (e.g, ARPES) are now accessible with increasing throughput, whereas the reliability of others, such as depth profiling, is improving. Finally, techniques like HAXPES implemented in the past only at synchrotron facilities, are now entering into laboratories.

In this talk I will illustrate by a series of examples in the field of device technology this evolution of surface analysis getting beyond traditional methods, driven by technological developments.

3:00pm **AS+BI+CA+LS-TuA-3 Core Levels Sub-shell Photo-ionization Cross-sections of Au, Ag, Cu in the Hard X-ray Photon Energy Range of 7-26 keV**, ***Germán Rafael Castro**, J Rubio Zuazo,* Spanich CRG BM25-SpLine Beamline at the ESRF, France

Hard X-ray Photo-electron spectroscopy (HAXPES)[1] has been developed in the last 10-15 years as a unique tool for retrieving accurate non-destructive[2] compositional and electronic bulk property of materials in the tens of nano-meters depth-scale with nano-meter resolution. Furthermore, the ability to tune the excitation energy in the hard X-ray regime enables tuning the sampling depth, i.e. depth profile analysis, but also enables the discrimination between bulk and surface effects, especially if combined with variable incident and exit angle.

However, an important drawback is the lack of knowledge of the photo-ionization cross-section at the HAXPES photon energy and in special for now accessible deeper core levels. Recently theoretical data has been reported [6] concerning the photo-ionization cross sections and parameters of the photo-electron angular distribution for atomic subshells but for binding energies lower than 1.5 keV of all elements with $1 \le Z \le 100$ in the photon energy range 1.5–10 keV. Unfortunately, these calculations do not contain information for deep orbitals accessible in HAXPES, even more there are scarce experimental results reported for both depth core levels and hard x-ray excitation energies.[3,4]

In the present work we will show the experimentally obtained relative sub-shell photo-ionization cross sections for 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f, 5s, 5p, 5d core levels of gold (Au), 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d core levels of silver (Ag) and 1s, 2s, 2p, 3s, 3p, 3d core levels of Cooper (Cu) in the X-ray photon energy range of 7–26 keV. In the case of Au, cross sections have been corrected with experimental obtained angular anisotropy parameter. A comparison with theoretical sub-shell photo-ionization cross sections, and angular anisotropy photo-inionization parameters [5,6] will be also presented.

References

1. J. Rubio-Zuazo, G.R. Castro, *Nucl. Instrum. Methods Phys. Res. A,* ***547****, 64-72 (2005)*.

2. J. Rubio-Zuazo, P. Ferrer, G.R. Castro, *J. Electron Spectrosc. Relat. Phenom.,* ***180****, 27-33 (2010)*.

3. M. Gorgoi, F.Schäfers, S.Svensson, N.Mårtensson," J. Electron Spectrosc. Relat. Phenom.,, **190**, 153-158 (2013)

4. C. Kunz, S. Thiess, B. Cowie, T.-L. Lee, J. Zegenhagen, *Instrum. Methods Phys. Res. A,* ***547****, 73-86 (2005)*.

5. J.H. Scofield, J. Electron Spectrosc. Relat. Phenom. **8** 129–137 (1976).

6. M.B. Trzhaskovskaya, and V.G. Yarzhemsky, At. Data and Nucl. Data Tables,**119** (2018) 99–174

3:20pm **AS+BI+CA+LS-TuA-4 Interfacial Photochemistry of Pyruvic Acid in Atmospheric Chemistry**, ***Yanjie Shen**, Y Fu,* Pacific Northwest National Laboratory*; X Yao,* Ocean University of China*; Z Zhu,* Pacific Northwest National Laboratory*; X Yu,* Earth and Biological Sciences Directorate

Presentation Summary:

This presentation will show our latest results of pyruvic acid photochemical aging in dry and liquid surface analysis s using time-of-flight secondary ion mass spectrometry.

Abstract

Pyruvic acid is widespread in fogs, aerosols, and clouds. The sunlight driven reaction pathways of pyruvic acid in the air-liquid interface are more elusive compared to its well-known gas and bulk phase chemistry in the atmosphere. We investigated photochemical aging products from pyruvic acid after different UV photolysis times up to 8 hours in dry and liquid samples using time-of-flight secondary ion mass spectrometry (ToF-SIMS). Both ToF-SIMS spectral and spectral principal component analysis (PCA) were used to study the surface photochemical aging products among various photochemical aging samples. A number of aging products were observed in dry samples indicating the importance of interfacial reactions[1]; however, the dry sample analysis cannot fully represent the air-liquid interfacial chemistry of pyruvic acid. Therefore, we used our unique liquid surface molecular imaging approach enabled by the SALVI microfluidic reactor to study the air-liquid interface. The *in situ* liquid SIMS observations show photochemical products of pyruvic acid at the air-liquid interface including oxidation products (i.e., acetic acid, oxalic acid, formic acid, lactic acid), oligomers (i.e., dimethyltartaric acid), and water clusters (i.e., $(H_2O)_nH^+$, $(H_2O)_nOH^-$) with submicrometer spatial resolution. In addition, SIMS three-dimensional chemical mapping provides visualization of the surface mixing state at the molecular level. For example, oligomers and oxidation products become more significant as illustrated in the chemical spatial mapping with increased photolysis time. Our study of the pyruvic acid aqueous surface provides new understanding of complex photochemical reactions as an important source of aqueous secondary organic aerosols (SOAs) in atmospheric chemistry.

Key Words: pyruvic acid, photochemical, dry SIMS, liquid SIMS, air-liquid interface, oligomer, water cluster, SOA.

References:

1.Fu, Y.; Zhang, Y.; Zhang, F.; Chen, J.; Zhu, Z.; Yu, X.-Y., Does interfacial photochemistry play a role in the photolysis of pyruvic acid in water? *Atmospheric Environment* **2018,***191*, 36-45.

4:20pm **AS+BI+CA+LS-TuA-7 Nanoscale Tomographic Mapping the Liquid-Solid Interface with Cryo-APT**, ***Daniel Perea**, D Schreiber, J Evans, J Ryan,* Pacific Northwest National Laboratory **INVITED**

The liquid-solid interface plays an essential role in many phenomena encountered in biological, chemical, and physical processes relevant to both fundamental and applied science. However, study of the liquid/solid interface at the nanoscale is challenging as liquids are generally incompatible with many analytical techniques that require high to ultrahigh vacuum conditions. One strategy to probe the liquid-solid interface is to cryogenically freeze the liquid into solid form to preserve local ionic chemistry gradients and surface composition within a solid structure, making it more amendable to vacuum-based analyses such as Atom Probe Tomography (APT). However, the regular application of APT to hydrated materials is lacking due to challenges in preparing the necessary nanoscale needle-shaped specimens using a FIB-SEM and the subsequent environmentally-protected transfer of the frozen specimens to the APT instrument for analysis. In this presentation, I will discuss the development of a FIB-based site-specific liftout and attachment scheme of cryogenically cooled specimens involving a combination of redeposition and overcoating of organic and organometallic molecules. A modified commercially-available specimen suitcase shuttle device and an environmental transfer hub vacuum chamber at PNNL is used to facilitate environmentally-protected specimen transfer between the cryo FIB and the APT tool, allowing for the first time, APT analysis of a water/solid interface in 3D to reveal the complex nanoscale water-filled porous network of corroded glass. Application of this unique specimen preparation approach to biological specimens will also be discussed.

5:00pm **AS+BI+CA+LS-TuA-9 Characterization of Electronic Materials using Low Energy Inverse Photoemission Spectroscopy**, ***Benjamin Schmidt**, J Newman, J Mann, K Artyushkova, L Swartz,* Physical Electronics*; M Terashima, T Miyayama,* ULVAC-PHI Inc., Japan

The development of complex electronic materials in areas such as batteries, solar cells, and flexible display panels require a detailed knowledge of the electronic band structure in order to achieve desired performance. A few of the material properties of interest are electron affinity, work function, ionization potential, and bandgap. Photoemission spectroscopic techniques such as Ultraviolet Photoelectron Spectroscopy (UPS) and Inverse Photoemission Spectroscopy (IPES) have traditionally been used to measure these values.

Organic electronic materials are growing in popularity due to lower costs of production and the ability to create interesting mechanical structures. However, they are susceptible to chemical damage with prolonged exposure to high-energy electron beams during analyses, which can affect the measured properties.

Low Energy Inverse Photoemission Spectroscopy (LEIPS) is a variant of IPES but uses an incident electron beam at lower energy than traditional IPES (< 5 eV vs. ~10 eV, respectively), making it less damaging for organic materials. In this talk, the operating principles of LEIPS will be discussed. Several material system examples will be shown, including films of C60 and copper phthalocyanine (CuPc).

5:20pm **AS+BI+CA+LS-TuA-10 Deconvolution of Atom Probe Tomography on Nanomaterials for Renewable Energy**, ***Margaret Fitzgerald***, *M Dzara, D Diercks,* Colorado School of Mines*; N Leick, S Christensen,* National Renewable Energy Laboratory*; T Gennett, S Pylypenko,* Colorado School of Mines

Technologies for hydrogen-based economy rely heavily on advancements in development of nano-structured materials. Nano-materials used in applications for energy conversion, storage and production have unique, desirable properties because of their intricate chemistries and morphologies, however this makes them difficult to characterize using traditional techniques. Of specific interest is elucidation of the surface properties and identification of differences between surface and bulk composition. This work features Atom Probe Tomography (APT) paired with other techniques that enable multi-scale characterization in 2D and 3D as a promising approach to create a more complete picture of the complexities of nano-structured materials.

APT is an incredibly powerful tool that has been used to render sub-nanometer-resolution, 3D reconstructions of metallic and, more recently, ceramic samples to enhance the understanding of local composition variations, such as around grain-boundaries and precipitates. This presentation outlines the procedures and considerations for expansion of APT towards analysis of nano-structured materials used for catalysis and hydrogen storage. Challenges related to both APT specimen preparation, APT analysis, and data reconstructions will be discussed. Specific considerations that will be addressed include sample pre-screening for mass spectrometry peak overlap, substrate and encapsulation material selection based on field evaporation compatibility, and prevention of sample damage for air- and beam-sensitive materials. In order to produce accurate 3D reconstructions of the APT data for these samples, initial assessment of a two-dimensional morphology of these materials is made using scanning transmission electron microscopy (STEM) and elemental distributions are acquired with energy dispersive x-ray spectroscopy (EDS). Surface chemistry of the sample is determined using X-ray Photoelectron Spectroscopy (XPS) in order to correlate surface chemistry between APT data and quantified XPS chemical ratios. This talk will provide evidence of cross-correlation across multiple techniques and integration of 2D and 3D data to provide a pathway for understanding these complex materials beyond traditional capabilities.

5:40pm **AS+BI+CA+LS-TuA-11 Mass Spectrometric Investigation of Ion Solvation in Liquids, a Comparison of *in situ* Liquid SIMS to Regular ESI-MS**, ***Yanyan Zhang***, Institute of Chemistry, Chinese Academy of Sciences, China*; D Baer, Z Zhu,* Pacific Northwest National Laboratory

Ion solvation plays very important roles in many important biological and environmental processes. Mass spectrometry (MS)-based methods have been used to investigate this topic with molecular insights. To study ion solvation, ionization processes should be as soft as possible in order to retain solvation structures. An *in situ* liquid secondary ion MS (SIMS) approach developed in our group has been recently utilized in investigations of Li ion solvation in nonaqueous solution, and it detected a series of solvated Li ions.[1] As traditionally SIMS has long been recognized as a hard ionization process with strong damage occurring at the sputtering interface, it is very interesting to study further how soft *in situ* liquid SIMS can be. In this work, we used halide ion hydration as a model system to compare the ionization performance of the *in situ* liquid SIMS approach with regular electrospray ionization MS (ESI-MS). Results show that, although ESI has been recognized as a soft ionization method, nearly no solvated halide ions were detected by regular ESI-MS analysis, and only strong signals of salt ion clusters were seen. As a comparison, in liquid SIMS spectra, a series of obvious hydrated halide ion compositions could be observed.[2] Our findings demonstrated that the *in situ* liquid SIMS approach is surprisingly soft, and it is expected to have very broad applications on investigation of various weak interactions and many other interesting chemical processes (e.g., the initial nucleation of nanoparticle formation) in liquid environment.

References:

[1] Zhang, Y.; Baer, D.; Zhu, Z.*, et al., "Investigation of Ion-Solvent Interactions in Non-Aqueous Electrolytes Using *in situ* Liquid SIMS", *Anal. Chem.*, **2018**, *90*, 3341–3348.

[2] Zhang, Y.; Zhu, Z.*, et al., "*In Situ* Liquid SIMS: A Surprisingly Soft Ionization Process for Investigation of Halide Ion Hydration", *Anal. Chem.***2019**, *published online,* DOI: 10.1021/acs.analchem.8b05804.

6:00pm **AS+BI+CA+LS-TuA-12 Characterizing the Thickness and Physical Properties of Nearly Ideal Zirconium Oxide Surfaces Using Ellipsometry, ESCA, Profilometry and FIB**, ***Edward Gillman***, Naval Nuclear Laboratory

Zirconium alloys are used in nuclear reactor cores due to their small neutron scattering cross-section and corrosion resistance. Corrosion of zirconium alloys results in the formation of a protective oxide layer that the corrosion species must travel through in order to continue the corrosion process. This oxide prevents further oxidation of the metal, slowing down the reaction rate. Characterizing this important oxide film on a metal is difficult. A number of analytical techniques are used to better understand the properties and growth of this oxide film. To insure that reliable information is reported, the thickness and physical properties of zirconium oxide deposited on a single-crystal silicon wafer by magnetron sputtering has been investigated. Data obtained from Electron Spectroscopy for Chemical Analysis (ESCA), profilometry, ellipsometry and Focused Ion Beam (FIB) experiments are all self-consistent with each other. This validates the utility of these measurements for the characterization of the oxide observed on metallic surfaces.

Biomaterial Interfaces Division
Room A120-121 - Session BI+AS-TuA

Biomolecules and Biophysics and Interfaces & Flash Session

Moderators: Markus Valtiner, Vienna University of Technology, Austria, Tobias Weidner, Aarhus University, Denmark

2:20pm **BI+AS-TuA-1 Electrochemical Surface Reactivity of Catechol Derivatives: Competitive Adsorption and Ion Effects**, ***Laila Moreno Ostertag***, *L Mears, D Dworschak, M Valtiner,* Vienna University of Technology, Austria

Catechols are molecules well known for their participation in important biological processes such as neurotransmission and bioadhesion. Their adhesive properties are of great interest for the development of biocompatible glues and coatings. In particular, L-3,4-dihydroxyphenylalanine (L-DOPA) has been found to play a defining role in the attachment of mussel feet to organic and inorganic surfaces in wet environments. Its electrochemistry has been widely studied, but the possibilities of many other catechols in this field remain largely unexplored, as is the effect of diverse ionic media in which their properties could be improved.

By using several electrochemical techniques and comparing to a well-known model system, we have obtained an understanding of the redox mechanisms involved in the interaction of these molecules at a metallic interface. Reaction parameters such as diffusion coefficients and reaction constants have been determined in different ionic media.

This fundamental insight allows us to set catechols in the context of their role within interfacial phenomena. Our approach enables the elucidation of free energies that characterize the energy landscape of adhesion processes at electrified interfaces, which can then bridge the gap between bulk electrochemistry and single-molecular surface-force analysis techniques. Full energy pathways can be drawn based on combined results and lead to a wide range of possibilities in the development of catechols for specific applications.

2:40pm **BI+AS-TuA-2 Direct Observation of Lysozyme Interaction with a Curved Lipid Membrane Surface by Sum Frequency Scattering Vibrational Spectroscopy**, ***Thaddeus Golbek***, Aarhus University, Denmark, Denmark*; H Okur, S Kulik, J Dedic, S Roke,* École Polytechnique Fédérale de Lausanne (EPFL), Switzerland*; T Weidner,* Aarhus University, Denmark

Highly ordered protein aggregates play a large role in many neurodegenerative and non-neuropathic disorders including type II diabetes, Alzheimer's, Parkinson's, prion, and Huntington's disease. Even though a causative link between the formation of protein aggregates and server diseases has been established, the molecular level-details of protein aggregation and cell membrane disruption are still underdeveloped. One of the most characterized proteins that has been used to model protein aggregation is hen egg-white lysozyme. While lysozyme has been extensively studied at model surfaces, it has not been well studied on curved, more realistic, surfaces. In order to observe lysozyme at a curved surface we applied sum frequency scattering (SFS) vibrational spectroscopy to probe the interface between the protein and the curved lipid model cell membrane surface. The model cell membrane was built upon 10% 1,2-dimyristoyl-*sn*-glycero-3-phospho-(1'-rac-glycerol) (DMPG) and 90% 1,2-

dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC) lipid nanodroplet emulsions, were the oil is *n*-hexadecane. SFS studies at the protein-lipid interface demonstrate that binding of lysozyme induces increased lipid monolayer order. An increase in acyl chain order determined by the ratio of the CH_3 symmetric and CH_2 asymmetric peak amplitudes and lipid head group orientation change from about 0˚ to greater than 60˚, determined by the increase is phosphate head group signal, suggests that lysozyme inserts into the lipid layer causing lipid dehydration and reorientation. The amide I SFS spectrum lysozyme interacting with the model cell lipid monolayer is also studied to observe the folding and ordering of the protein. Altogether, we demonstrate the use of lipid monolayer nanodroplet emulsions as a platform to study protein membrane interactions in solution, which excludes air form the model further increasing biomimetic modeling potential using SFS.

3:00pm **BI+AS-TuA-3 Iron Speciation at Aqueous Surfaces***, **Heather Allen**,* Ohio State University **INVITED**

Ion pairing and speciation in the condensed phase and at the aqueous surface is presented for mono and multi-valent ions including iron and phosphate systems. We present new evidence of iron (III) surface prevalence at both the water and glycerol surfaces. Understanding surface water solvation structure using polarized Raman and vibrational sum frequency generation spectroscopy are also discussed.

4:20pm **BI+AS-TuA-7 Identifying the Molecular Mechanisms that Mediate Cell Membrane Repair by Sum Frequency Generation Spectroscopy***, T Golbek,* Oregon State University*; S Roeters, T Weidner,* Aarhus University, Denmark*; C Johnson, **Joe Baio**,* Oregon State University

Movement in everyday life places stress on sarcolemma which creates small tears in the muscle cell membrane. Mutations in this multi-domain dysferlin protein render it unable to repair the membrane and this phenomena is related to diseases such as specific forms of muscular dystrophy. Of particular importance is the moment after the release of calcium from tears in the muscle cell membrane, whereby the release of calcium triggers the C2A domain of dysferlin to dock with a lipid vesicle. Mutations mapped to this domain cause loss of binding ability of the C2A domain. This is the first step of muscle cell membrane repair, therefore there is a crucial need to understand the geometry of dysferlin C2A at a membrane interface as well as cell membrane lipid reorientation when compared to a variant. Here we describe a comparison between the wild type dysferlin C2A and a mutation to the conserved aspartic acids on the domains binding loops. To identify both the geometry and the cell membrane lipid reorientation, we applied sum frequency generation (SFG) vibrational spectroscopy and coupled it with simulated SFG spectra to observe and quantify the interaction. A model cell membrane was built with phosphotidylserine and phosphotidylcholine. Observed changes in surface pressure demonstrate that calcium bridged electrostatic interactions govern the initial interaction of the C2A domains docking with a lipid membrane. SFG spectra taken from the amide I region for wild type and variant contain features near 1642 cm^{-1}, 1663 cm^{-1}, and 1675 cm^{-1} related to the C2A domains beta-sandwich secondary structure indicates that the domain binds in a specific orientation. Mapping simulated SFG spectra to the experimentally collected spectra indicated that both wild type and variant domains have nearly the same orientation to the membrane surface. However, examining the ordering of the lipids that make up a model membrane using SFG, we find that the wild type clusters the lipids as seen by the ratio of the CD3 and CD2 symmetric intensities increases by 170% for the wild type and by 120% for the variant. This study demonstrates and highlights the capabilities of SFG to probe with great detail biological mutations in proteins at cell membrane interfaces.

4:40pm **BI+AS-TuA-8 Fishing Manganese out from Cellulose: Impact of Coupling Desferrioxamine B to Stainless Steel Beads on the Circular Economy of Paper and Pulp Industry***, **Jeff Wilkesman**,* Mannheim University of Applied Sciences, Germany*; K Mörtter, I Sommer, P Kunz,* Mannheim University of Applied Sciences, Deutschland

Important as an essential trace element with abundant applications, manganese (Mn) is rising attention due to its aesthetic, operational and health problems at higher concentration in the paper and water industry. When oxygen-containing paper bleaching chemicals (O_2, O_3, H_2O_2 or peracids) are used, the presence of heavy metals like Mn causes problems in the pulp processing, increasing the consumption of the bleaching chemicals and deteriorating pulp quality, including pulp darkening. An effective way to remove Mn from pulp is employing chelators, although its effectiveness is influenced by the overall water chemistry and concomitant contaminants. Successful chelation of Mn usually occurs at pH<8, otherwise highly oxidized species would form, precipitating insoluble Mn(III/IV) oxide minerals, and binding strongly to the pulp. Though the environmentally critical EDTA is used in the paper industry to chelate heavy metals, friendlier and greener alternatives are sought, like desferrioxamine B (DFOB) or E (DFOE), which are linear trihydroxamic acid siderophores produced by bacteria to acquire primarily Fe(III), but also Mn(II/III). Advantages of employing siderophores are its commercial availability, high solubility and stability over a wide pH range. The coupling of DFOB to ~3-4 mm stainless steel beads as solid support was performed. The beads were incubated overnight with several cellulose suspensions to allow formation of the Mn-DFOB complex (log *K* ~29.9). Control assays were performed using EDTA. After treatment, cellulose suspensions originally containing ~30–40 mg Mn/kg, were submitted for Mn(II), Mn(III) analysis, employing the TCPP [Tetrakis(4-carboxyphenyl)porphyrin] method. Total Mn content was also determined by Inductively Coupled Plasma (ICP). Preliminary results show an approximate 80% reduction of Mn content from the cellulose suspension, though experimentation is still carried on; DFOE is planned to be also analyzed. Mn was recovered by decoupling from DFOB by metal exchange and the beads were reused for further activation with DFOB. This removal alternative resulted in a feasible, easy, greener and economical procedure, leading for improvement in the paper industry. Still, the most expedient option comprising circular economy statements based on sustainable management parameters (cost-effectiveness, performance, simplicity) must be deeper explored. Clearly, further research regarding Mn(II/III) formation and removal will help the water and paper industry, by developing better methods to diminish Mn oxide deposits in pipe networks and optimizing the paper bleaching process, ultimately reducing significant operational costs.

5:00pm **BI+AS-TuA-9 The Hybrid Nano-biointerfaces Between Gold, Graphene Oxide and Angiogenin for Wound Repair***, **Diego La Mendola**,* University of Pisa, Italy*; L Cucci, G Villaggio, C Satriano,* University of Catania, Italy

Angiogenin (ANG) is a member of the ribonuclease family and a physiological constituent of the human plasma. Ang is a potent angiogenic factor regulating a wide range of responses, such as angiogenesis, cell proliferation, cell migration, and pro-survival effects. ANG has been shown related to many pathophysiological processes, including cancers, neurodegeneration, inflammation and regeneration of damaged tissues. In this work, we investigated a hybrid obtained by the assembly of ANG to gold nanoparticles and graphene oxide nanosheets, to exploit the synergic effects of antioxidant AuNP and antimicrobial GO, respectively. Au-GO-ANG were characterized by UV-visible spectroscopy, to correlate the changes in the plasmonic peak as well as in the π-->π* transitions to the protein interaction with Au and GO, respectively. QCM-D measurements on supported lipid bilayers, as model of cell membranes, pointed to a stronger interaction of the AuNP-Ang systems in comparison with the uncoated nanoparticles. The developed systems promoted fibroblasts migration and wound closure. Confocal microscopy cell imaging evidenced dynamic processes at the level of cytoskeleton and sub-cellular compartments. The results reveal a promising multifunctional platform for wound care treatment and tissue regeneration.

5:20pm **BI+AS-TuA-10 Improved Antibacterial Sandwich system for Urological Purposes***, **Sara Bröskamp**, G Franz,* Munich University of Applied Sciences, Germany*; D Jocham,* University Hospital of Schleswig-Holstein, Germany

In the anaerobic environment of kidneys and bladder which even lack the permanent presence of weak but always toxic oxidative reagents (like ClO_2^-) it is obvious that no Ag^+ ions can be generated by oxidation of a metallic silver film. However, it is well known that the antibacterial impact of Ag^+ ions which can act as a single ion is much higher than the effect of neutral silver nanoparticles [1]. In our efforts to define an effective membrane which is deposited on the interior and exterior surfaces of tubes which exhibit an aspect ratio of more than 100 (balloon catheters) we introduce a significantly improved coating which makes use of the soft oxidation of already deposited silver layers by a microwave or RF plasma [2]. This procedure not only improves the antibacterial effect but also extends the active time of the catheters. The silver oxide on top of the base silver layer which is deposited on an originally hydrophobic surface of an organic polymer by a well-known process is eventually topped by an organic layer of comparable thickness [3,4]. This coating with even thickness on the interior of the tubes has been extensively improved by a device which counteracts the decreasing vapor density of the film-building species by a well-definded temperature gradient [5]. In the case of ureteral stents, we make use of the series of drainage holes along the catheter which act as adjacent sources for the film-building monomer. This layer controls the antibacterial activity which can be effectively tuned by its porosity [6]. The oxidation of the silver also effectively prevents sulfidation by S-containing amino acids (cysteine) which can be present in the kidneys of patients. The silver release rate has been measured by atomic absorption spectroscopy (AAS).

[1] Heidari Zare, V. Juhart, A. Vass, G. Franz, and D. Jocham; Biointerphases 12, 011001 (2017).

[2] G. Franz, S. Bröskamp, K. Resch, W. Hiemeyer, D. Jocham; German patent disclosure DE 10 2019 001 994.6, Mar 26, 2019.

[3] G. Franz, F. Schamberger, A. Kutschera, S. Seyedi, D. Jocham, German patent disclosure DE 102012023349.3, Nov. 29, 2012.

[4] G. Franz, F. Schamberger, H. Heidari Zare, S.F. Bröskamp, and D. Jocham; Beilstein J. Nanotechn. 8, 1982 (2017). [5] S. Bröskamp, D. Redka, A. Möhlmann, G. Franz, and D. Jocham; AIP Advances 7, 075005(2017).

[6] F. Schamberger, A. Ziegler, and G. Franz, J. Vac. Sci. Technol. B30, 01801 (2012).

5:40pm **BI+AS-TuA-11 Quantitative Characterization of Piezoelectric Property in Biological System via Piezoresponse Force Microscopy***, **Jinha Kwon**, D Kim, H Cho,* The Ohio State University

Piezoresponse force microscopy (PFM) is a variant of scanning probe microscopic technique based on atomic force microscopy (AFM) that allows imaging of piezoelectric material domains with high resolution. This is achieved by keeping a sharp conductive probe in contact with a piezoelectric material and applying an alternating current (AC) directly to the sample through the probe, which results in deflection of the probe detected through photodiode detector. PFM has been successfully applied to many biological materials such as teeth [1], bone [2], seashell [3], and collagen fibrils [4]. Although biological samples are commonly vulnerable to high voltage input, previous studies used a high voltage input more than 10V to induce a piezoelectric strain large enough to be captured by an AFM tip [5]. Moreover, previous works did not carefully scrutinize the effect of substrate's conductivity and the contribution of parasitic electrostatic forces between the tip and sample, which should be precisely examined to obtain the quantitative piezoelectric properties of sample. In this study, we used type I collagen fibril which has weak piezoelectricity around 1 pm/V. The collagen fibril was aligned to the probe perpendicularly and AC voltage was applied to the fibril through the conductive AFM tip which was carefully calibrated in both vertical and lateral directions. In order to amplify its piezoresponse signal with a small electrical input, we utilized the contact resonance of an AFM cantilever. We also carefully examined the effect of substrate's conductivity by comparing piezoelectric response of the collagen on bare and gold-coated glass slides. Moreover, the contribution of electrostatic forces to the PFM results were investigated while they are varied by applying different DC offsets simultaneously to compensate the electrostatic force. Finally, the piezoelectric property of the collagen was calculated by fitting the measured piezoresponse vs. applied voltage graph. As a result, the piezoelectric properties of a single collagen fibril were precisely characterized in both vertical and shear directions and its heterogeneous nature within a fibril was revealed.

[1] S.V. Kalinin, B.J. Rodriguez, J. Shin, S. Jesse, V. Grichko, T. Thundat, A.P. Baddorf, A. Gruverman, Bioelectromechanical imaging by scanning probe microscopy: Galvani's experiment at the nanoscale, Ultramicroscopy. 106 (2006) 334–340.

[2] M. Minary-Jolandan, M.-F. Yu, Shear piezoelectricity in bone at the nanoscale, Appl. Phys. Lett. 97 (2010) 153127.

[3] T. Li, K. Zeng, Nanoscale piezoelectric and ferroelectric behaviors of seashell by piezoresponse force microscopy, J. Appl. Phys. 113 (2013) 187202.

[4] M. Minary-Jolandan, M.-F. Yu, Nanoscale characterization of isolated individual type I collagen fibrils: polarization and piezoelectricity, Nanotechnology. 20 (2009) 085706.

[5] D. Denning, J.I. Kilpatrick, E. Fukada, N. Zhang, S. Habelitz, A. Fertala, M.D. Gilchrist, Y. Zhang, S.A.M. Tofail, B.J. Rodriguez, Piezoelectric Tensor of Collagen Fibrils Determined at the Nanoscale, ACS Biomater. Sci. Eng. 3 (2017) 929–935.

Energy Transition Focus Topic
Room A226 - Session TL+AS+SS+TF-TuA

Breakthroughs and Challenges in Applied Materials for Energy Transition (ALL INVITED SESSION) & Panel Discussion

Moderators: Jason Avila, U.S. Naval Research Laboratory, Devika Choudhury, Argonne National Laboratory

2:20pm **TL+AS+SS+TF-TuA-1 Interface Science and Engineering for Energy-Water Systems***, **Seth Darling**,* Argonne National Laboratory **INVITED**

Driven by climate change, population growth, development, urbanization, and other factors, water crises represent the greatest global risk in the coming decades. Advances in materials represent a powerful tool to address many of these challenges. Understanding—and ultimately controlling—interfaces between materials and water are pivotal [1]. In this presentation, we will lay out the challenges and present several examples based on materials science strategies for addressing applications in water. In each instance, manipulation of interfacial properties provides novel functionality, ranging from selective transport to energy transduction to pollution mitigation.

[1] J. Appl. Phys. 124 (2018) 030901

3:00pm **TL+AS+SS+TF-TuA-3 Atomic Dynamics of Noble Metal Surface in Gases Revealed by Time Resolved Environmental Transmission Electron Microscopy***, **Seiji Takeda**, N Kamiuchi, R Aso, H Yoshida, T Tamaoka,* Osaka University, Japan **INVITED**

The surface of noble metals in gas has been extensively studied in the field of surface science. The surface has been investigated in both ultra high vacuum and various gases of high pressure and under various stimuli, for instance the illumination of intense light, the electric and/or magnetic field and the irradiation of charged particles. A microscopy study is potentially useful to provide us with the imaging data on the surface in real space and time at the resolution that is available in a microscopy apparatus to use. Among various methodologies for microscopy, atomic resolution environmental transmission electron microscopy has advanced greatly in the time resolution recently, allowing us to explore the dynamic surface and to elucidate the mechanism of the dynamic phenomena that are related to various energy transition processes. We show recent our studies, including the self-activated surface dynamics of gold catalysts in reaction environments [1] and the unexpected gas (nitrogen) -solid (palladium) transition [2] that is occurring on the surface under a strong electrostatic field. We demonstrate that the surface dynamics that is associated with the energy transition processes needs to be visualized at atomic scale for understanding the electronic excitations behind the surface dynamics.

References

[1] N. Kamiuchi et al., Nat. Commun. **9** (2018) 2060.

[2] T. Tamaoka, R. Aso et al., Nanoscale (2019) .

4:20pm **TL+AS+SS+TF-TuA-7 Totally Organic and Organic-Inorganic Hybrid Batteries***, **Burak Esat**,* Fatih University, Turkey, Rutgers University*; S Bahceci, S Akay,* Fatih University, Turkey*; A Momchilov,* Bulgarian Academy of Science, Bulgaria

We hereby represent novel polymers and reduced graphene oxide with pendant electro-active groups such as TEMPO and quinones.

The first example of polymers with pendant anode-active groups studied in our group is a polymethacrylate derivative carrying anthraquinone moieties (pMAntrq). This anthraquinone based anode-active material has proven to show a quite good reversible electrochemical reduction behavior in both aqueous and non-aqueous electrolytes in our studies. pMAntrq|1M $LiClO_4$ in EC:DEC=1:1|Li battery system has been constructed. The initial discharge capacity of the cell obtained was 151 mAh/g when cycled between 4.2 and 1.2V at 0.25C rate and 79.2 mAh/g when cycled between 4.0 and 1.5V at 0.3C rate during subsequent cycles.

This material was also used in an aqueous battery, pMAntrq |5M KOH aq.|$LiMn_2O_4$. Although an initial discharge capacity of 37.7 mAh/g was obtained, it deteriorated quickly due to the solubility of the reduced form of the polymer in this electrolyte system. This is the first reported example of such organic-inorganic hybrid battery.

An anode material based on reduced graphene oxide (RGO) functionalized with anthraquinone is also investigated and a battery against Li metal revealed a quite reversible capacity of 200 mAh/g based on the weight of electro-active anthraquinone moieties when cycled between 3.2 and 1.8 V at 0.3C rate. The energy density was found to be around 450 mWh/g.

We have also synthesized and characterized polyacetylene polymers with pendant TEMPO radicals which are electrochemically oxidizable in a reversible manner at around 3.5-3.6V vs. Li. These materials have been proven to be cathode-active materials for rechargeable batteries. We have demonstrated that a mixture of Tempo radical polymer with $LiMn_2O_4$ (1:1) can be used as a hybrid cathode material. Typically, this polymer may be expected to act as a polymeric electro-active binder and a stability improver for the inorganic cathode-active material.

Studies toward construction of all organic batteries using these anode and cathode materials are currently in progress.

4:40pm **TL+AS+SS+TF-TuA-8 Electrochemical Strategies for Designing Interfaces of Battery Materials***, **Betar Gallant**,* Massachusetts Institute of Technology **INVITED**

Future generations of energy-storage devices require advances beyond state-of-the-art materials and redox systems. Rechargeable batteries, specifically today's Li-ion batteries, have largely been dominated by transition metal oxide cathodes; advanced conversion systems with higher theoretical energy densities, such as Li-S and Li-O_2, have received significant attention as "beyond Li-ion" batteries, but have their own challenges and limitations. Looking at the periodic table invites one to wonder, "Is there more beyond sulfur and O_2?" This talk will focus on challenges and opportunities related to a different chemical family: fluorine, or more specifically, active fluoride. Fluoride-containing additives, electrolytes, solid electrolyte interphases (SEI), and intercalation materials represent a recurring motif in many proposed next-generation battery chemistries, but current understanding of the behavior of fluorinated interfaces and materials remains largely phenomenological. In addition, controlling the incorporation of fluoride into materials still remains a major challenge owing to safety issues of fluorine and the intransigence of fluoride-containing precursors, hindering design in this space.

In this talk, I describe our group's exploration of several applications where fluoride-forming reactions can be harnessed and tailored for benefit in advanced batteries. First, I describe our efforts to develop high-energy density redox systems based on the electrochemical reduction of fluorinated gases. We show that fundamental knowledge and the experimental framework developed in the field of Li-O_2batteries in recent years can be successfully translated to the development of new gas-to-solid conversion reactions with high energy densities. Next, I will discuss the opportunities presented by the ability to generate fluoride *in situ* in working batteries from these reactions, creating new possibilities to fluorinate interfaces in tailorable and precise ways. I will present our findings relevant to two examples where fluoride has been suggested to play a critical and enabling role: Li anode interfaces, and oxyfluoride-based intercalation cathodes. Using our gas-based fluoridation architecture, we explore the fundamental role that fluoride plays in each of these applications. Finally, I will highlight future challenges and opportunities in the characterization of fluoridated materials.

2D Materials

Room A216 - Session 2D+AS+MI+NS-WeM

2D Materials Characterization by Scanning Probe Microscopy and Spectroscopy

Moderator: Ivan Oleynik, University of South Florida

8:00am **2D+AS+MI+NS-WeM-1 Plasmon Induced Excitation of Doublet Emission at the Single Molecule Level*, Alberto Martin-Jimenez,* *K Lauwaet,* IMDEA Nanoscience, Spain*; P Merino, J Martinez,* ICMM-CSIC, Spain*; R Miranda, R Otero,* IMDEA Nanoscience, Spain

In this contribution we report a careful investigation of the topographic, electronic, and opto-electronic properties of electronically decoupled C60 nanocrystals by means of Scanning Tunneling Microscopy (STM), Scanning Tunneling Spectroscopy (STS), STM induced Light Emission (STM-LE), and Density Functional Theory (DFT), at the single molecule level. We have observed that depending on the tunneling parameters, we are able to reversibly switch from a broad plasmonic spectrum to a series of very sharp molecular resonances of 10meV width. Based on our STS data and DFT calculations we have reached a model to explain the molecular light emission of the C60 nanocrystals. We demonstrate that the emission arises from the recombination of a doublet exciton of negatively charged molecules (anions). Our results will contribute to the general understanding of the physical mechanisms involved in the light emission of organic molecules. They may also be of importance for applications such as single photon emitters or quantum computing, since future devices may need to be able to switch chromaticity in a controlled fashion.

8:20am **2D+AS+MI+NS-WeM-2 Silicene like Domains on $IrSi_3$ Crystallites***, **Nuri Oncel**, D Cakir, F Fatima, D Nicholls,* University of North Dakota

Recently, silicene, the graphene equivalent of silicon, has attracted a lot of attention due to its compatibility with Si-based electronics. So far, silicene has been epitaxially grown on various crystalline surfaces such as Ag(110), Ag(111), Ir(111), ZrB_2(0001) and Au(110) substrates. Here, we present a new method to grow silicene via high temperature surface reconstruction of hexagonal $IrSi_3$ nanocrystals. The h-$IrSi_3$ nanocrystals are formed by annealing thin Ir layers on Si(111) surface. A detailed analysis of the STM images shows the formation of silicene like domains on the surface of some of the $IrSi_3$ crystallites. We studied both morphology and electronic properties of these domains by using both scanning tunneling microscopy/spectroscopy and first-principles calculation methods.

8:40am **2D+AS+MI+NS-WeM-3 Interfacial and Topological Superconductivity in 2D Layers Studied by Spin-Resolved Scanning Tunneling Spectroscopy***, **Roland Wiesendanger**,* University of Hamburg, Germany **INVITED**

In this presentation, we will first focus on interfacial superconductivity in novel types of heterostructures. In particular, we will present a low-temperature SP-STS study of ultrathin FeTe1-xSex (x = 0, 0.5) films grown on prototypical Bi-based bulk topological insulators. We observe fully developed U-shaped superconducting gaps in FeTe0.5Se0.5 layers of one unit cell (UC) thickness with a transition temperature (Tc) of ~11 K, close to the one of the corresponding bulk system (Tc ~ 14.5 K) [1]. Surprisingly, we also find clear evidence for superconductivity up to Tc ~ 6 K for one UC thick FeTe layers grown on Bi2Te3 substrates [2], in contrast to the non-superconducting FeTe bulk compound which exhibits bicollinear antiferromagnetic (AFM) order in a wide temperature range up to 70 K. Even more surprisingly, detailed investigations of the atomic-scale spin-resolved local density of states by SP-STS reveal that superconductivity in one UC layers of FeTe grown on Bi2Te3 appears to spatially coexist with bi-collinear AFM order. By using 3D-vector-resolved SP-STM techniques [3] we find an unusual reorientation of the diagonal double-stripe spin structure at Fe1+yTe thin film surfaces [4]. Moreover, variable-temperature SP-STM studies [5] reveal an enhanced Néel temperature for AFM spin ordering of the ultrathin FeTe films grown on topological insulators [6]. These findings open novel perspectives for theoretical studies of competing orders in Fe-based superconductors as well as for experimental investigations of exotic phases in heterostructures of topological insulators and superconducting layers.

In a second part, we will address experimental and theoretical studies of monolayer topological superconductivity and chiral Majorana edge modes in model-type 2D magnetic Fe islands on elemental superconducting Re [7]. In particular, we demonstrate that interface engineering by an atomically thin oxide layer is crucial for driving the studied hybrid system into a topologically non-trivial state as confirmed by theoretical calculations of the topological invariant, the Chern number.

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[1] A. Kamlapure et al., Phys. Rev. B 95, 104509 (2017).

[2] S. Manna et al., Nature Commun. 8, 14074 (2017).

[3] S. Meckler et al., Rev. Sci. Instrum. 80, 023708 (2009).

[4] T. Hänke et al., Nature Commun. 8, 13939 (2017).

[5] J. Warmuth et al., NPG Quantum Materials 3, 21 (2018).

[6] U. R. Singh et al., Phys. Rev. B 97, 144513 (2018).

[7] A. Palacio-Morales, E. Mascot, S. Cocklin, H. Kim, S. Rachel, D. K. Morr, and R. Wiesendanger, arXiv:1809.04503 (2018).

9:20am **2D+AS+MI+NS-WeM-5 Geometric Imaging of Borophene Polymorphs***, **Xiaolong Liu**,* Northwestern University*; L Wang,* Rice University*; S Li, M Rahn,* Northwestern University*; B Yakobson,* Rice University*; M Hersam,* Northwestern University

Two-dimensional (2D) boron, known as borophene, has recently been experimentally realized[1,2] revealing a number of polymorphic structures. A common characteristic of those borophene polymorphs is the presence of hollow-hexagons (HH) in an otherwise triangular lattice. The vast number of possible HH lattices underlies the polymorphic nature of borophene. Superlattices of HHs could be further realized when borophene phases periodically intermix in the form of line defects[3]. While scanning tunneling microscopy (STM) of borophene with conventional metal probes has revealed key features of borophene, significant ambiguity of the exact atomic lattice structure exists due to the convolution of electronic and structural details. With CO-functionalized atomic force microscopy, we unambiguously resolve the HH lattice and reveal features corresponding to B-B covalent bonds[4] that are supported by numerical simulations. We further show that CO-functionalized STM is an equivalent but more accessible technique for HH imaging, allowing us to assemble a growth phase diagram of borophene involving non-rotated, 30°-rotated and randomly rotated borophene phases on Ag(111), confirming the $v_{1/5}$ and $v_{1/6}$ models as the unifying structures for all observed phases. In particular, a transition from rotationally commensurate to incommensurate phases is observed at high growth temperatures, corroborating the chemically discrete nature of borophene.

*Current affiliation of Xiaolong Liu: Kavli Postdoc Fellow, LASSP, Cornell University

1. A. J. Mannix, X.-F. Zhou, B. Kiraly, J. D. Wood, D. Alducin, B. D. Myers, X. Liu, B. L. Fisher, U. Santiago, J. R. Guest, M. J. Yacaman, A. Ponce, A. R. Oganov, M. C. Hersam, N. P. Guisinger, *Science* **350**, 1513–1516 (2015).

2. B. Feng, J. Zhang, Q. Zhong, W. Li, S. Li, H. Li, P. Cheng, S. Meng, L. Chen, K. Wu, *Nat. Chem.* **8**, 563–568 (2016).

3. X. Liu, Z. Zhang, L. Wang, B. I. Yakobson, and M. C. Hersam, *Nat. Mater.***17**, 783–788 (2018).

4. X. Liu, L. Wang, S. Li, M. S. Rahn, B. I. Yakobson, and M. C. Hersam, *Nat. Commun.* **10**, 1642 (2019).

9:40am **2D+AS+MI+NS-WeM-6 Atomic Manipulation of Defects in the Layered Semiconductor 2H-$MoTe_2$***, **Sara Mueller**, S Deng,* The Ohio State University*; B St. Laurent,* University of New Hampshire*; Y Wang, W Windl,* The Ohio State University*; S Hollen,* University of New Hampshire*; J Gupta,* The Ohio State University

Here we present a charge control of native defects in the bulk transition metal dichalcogenide, $MoTe_2$ by scanning tunneling microscopy (STM). Bulk $MoTe_2$ was cleaved at room temperature in ultrahigh vacuum and imaged with a cut PtIr tip at 9K. Native defects in the $MoTe_2$ are present throughout the sample and image with complex structure. In topographic imaging, the long-range protrusion of a bright defect indicates the species is charged and we image the defects at different depths below the surface. They present with an ionization feature in tunneling spectroscopic mapping which indicates that the charge state of this defect can be manipulated by the band bending caused by the tip. Voltage pulses from the tip migrate the subsurface defects to the surface layer. The migrated defects present with the same spectroscopic signature as native surface defects. We also present DFT results that we use to clarify the identification of these native defects and energy barriers for migration between layers of 2H-$MoTe_2$.

11:00am **2D+AS+MI+NS-WeM-10 Scanning Tunneling Microscopy and Spectroscopy of a Heterotriangulene-based 2D Polymer**, ***Zachery Enderson***, *H Murali, R Dasari, T Parker, S Marder, H Li, Q Dai, S Thomas, J Brédas, P First,* Georgia Institute of Technology

Covalent Organic Frameworks (COFs) and similar materials synthesized from bottom-up procedures grant scientists a means to customize a 2D material's final properties from its initial precursors. The dimethylmethylene-bridged triphenylamine (DTPA) COF is an excellent example of the unique systems one can fabricate with these techniques[1]. The DTPA COF is initially synthesized on Au(111) or Ag(111) which facilitates crystalline growth through Ullman-type coupling. With an even number of electrons per unit cell, theory predicts a semiconducting electronic structure for the COF. Further heating in vacuum selectively cleaves the dimethyl groups but leaves the framework intact. This final COF resembles an ultra-flat covalent network of triangulene molecules with enticing proposed electronic properties, which depend on how the demethylated sites are terminated. In the case of hydrogen termination at these sites, calculations indicate that the "radical" COF on a metallic substrate will be a half-metal (fully spin-polarized density of states at the fermi energy)[2]. Using a low-temperature scanning tunneling microscope, the work outlined in this talk presents new information on the electronic structure of the DTPA COF in both its intact (methylated) and radical (demethylated) forms.

[1] Bieri, Marco, Stephan Blankenburg, Milan Kivala, Carlo A. Pignedoli, Pascal Ruffieux, Klaus Müllen, and Roman Fasel. "Surface-Supported 2D Heterotriangulene Polymers." *Chem. Commun.* 47, no. 37 (2011): 10239–41. https://doi.org/10.1039/C1CC12490K .

[2] Kan, Erjun, Wei Hu, Chuanyun Xiao, Ruifeng Lu, Kaiming Deng, Jinlong Yang, and Haibin Su. "Half-Metallicity in Organic Single Porous Sheets." *Journal of the American Chemical Society* 134, no. 13 (April 4, 2012): 5718–21. https://doi.org/10.1021/ja210822c .

11:20am **2D+AS+MI+NS-WeM-11 Scanning Tunneling Microscopy Investigations of Molecules Adsrobed on Semiconducting Graphene Nanoribbons**, ***Sineth Premarathna***, *K Latt, S Hla,* Ohio University

Unlike graphene, semiconducting graphene nanoribbons poccess a band gap and they have the capability to electronic decouple the molecules from the supporting substrate. Here, we study the structural, electronic and vibrational properties of individual para-sexiphenyl molecules adsorbed on semiconducting graphene nanoribbons. The graphene nanoribbons here are grown on the surface of Au(111) using DBBA molecules as the initial building blocks. Para-sexiphenyl molecules adsorb on the graphene naribbons with their long molecular axis positioning parallel to the long axis of the graphene nanoribbons. As expected, the tunneling spectroscopy data reveal the HOMO-LUMO gap of the molecule on graphene nanoribbons much closer to their gas phase values. Moreover, teh vibration spectroscopy measurements of the molecules further provide a strong vibration mode associate with the C=C ring stretching of the molecules. This work provide single molecule level information on the electronic, vibronic and structural properties of the molecules adsorbed on vertically stacked heterostructures formed by graphene nanoribbons on Au(111) surface.

Acknowledgement: This work is supported by the DOE-BES, DE-FG02-02ER46012 grant.

11:40am **2D+AS+MI+NS-WeM-12 Molecular Flexure and Atom Trapping with Sexiphenyl Molecules by Scanning Tunneling Microscope Manipulation**, *Y Zhang,* ***Shaoze Wang***, *K Braun, S Hla,* Ohio University

Molecular flexure, and molecule-metal contact of para-sexiphenyl molecules on a Ag(111) surface are investigated by using low temperature scanning tunneling microscopy, and molecular manipulations. Atom trapping with sexiphenyl molecules is realized by laterally manipulating the molecules onto individual silver atoms and up to three silver atoms have been trapped. We also demonstrate breaking of a silver dimer into individual silver atoms by atom trapping. STM manipulation experiments show that the molecule-metal complexes formed by the atom trapping are mechanically stable. Moreover, lateral manipulation of a single seziphenyl across a Ag(111) atomic step highlights how the molecule moves across step-edges; the molecule can easily conform across the step and it recovers original configuration after the manipulation.

Acknowledgement: This woek is supported by the DOE-BES, DE-FG02-02ER46012 grant.

12:00pm **2D+AS+MI+NS-WeM-13 Localized Strain Effects in Spin-Polarized Density of States for 2D-MnGaN – a Room Temperature Ferromagnetic Monolayer**, *Y Ma,* Ohio University*; K Meng,* The Ohio State University*; D Hunt, M Barral, V Ferrari,* CAC-CNEA, Argentina*; F Yang,* The Ohio State University*;* ***Arthur Smith***, Ohio University

We recently demonstrated the first observation of a 2D *room-temperature-ferromagnetic monolayer* of MnGaN (2D-MnGaN) using spin-polarized scanning tunneling microscopy and spectroscopy. The sample is grown by molecular beam epitaxy on gallium nitride substrates. We resolved ferromagnetic domains using SP-STM, demonstrated magnetic hysteresis using small *out-of-plane* magnetic fields, observed magnetic rim states, and measured magnetic DOS profiles using tunneling spectroscopy which are in excellent agreement with the predicted spin-polarized & spin-split DOS peaks obtained from first-principles theory. This work was published online in December 2017 in *Nano Letters*.[1]

More recently, we are investigating the dependence of magnetization anisotropy on *in-plane* lattice strain. First of all, we have observed from the spectroscopy measurements that the position of the spin-polarized Mn DOS peak varies from spectrum to spectrum, ranging from -1.69 eV up to -1.22 eV (relative to E_Fermi). In order to investigate if these variations could be related to structural variations, we have also carried out theoretical calculations based on first principles for both isotropic and local anisotropic lattice strains. The isotropic strain case shows that the occupied-states Mn peak can indeed shift by many tenths of an eV if the 2D-MnGaN is strained *in-plane*; for example, E = -1.58 eV for the no-strain case, whereas E = -1.33 eV for tensile strain (+9.1%) and E = -2.22 eV for compressive strain (-6.0%). On the other hand, we find an opposite behavior in the local anisotropic calculation.

Using atomic resolution STM, we have also found that significant strain variations exist within the 2D-MnGaN. As compared to an ideally periodic hexagonal lattice, the 2D-MnGaN lattice displays local spacing variations, and the spacing distribution is highly non-Gaussian and may instead be characterized as *tri-modal* with the central peak matching closely the expected average for 2D-MnGaN of 5.52 Å, but with left and right peaks centered around 5.00 Å and 5.92 Å. Therefore, the Mn atoms, centered between Ga adatoms, are under highly varying strains, ranging from tensile to compressive.

By mapping the observed Mn peak energies onto theoretical energy-strain curves, we can then estimate the expected lattice parameters corresponding to particular energies and compare with the lattice spacing distribution. These results will be discussed as well as the additional discovery of a dependence of the spin anisotropy on the lattice strain.

[1] *Yingqiao Ma, Abhijit V. Chinchore, Arthur R. Smith, María Andrea Barral, and Valeria Ferrari, Nano Letters* ***18****, 158 (2018).*

Biomaterial Interfaces Division
Room A120-121 - Session BI+AS-WeM

Microbes and Fouling at Surfaces

Moderators: David G. Castner, University of Washington, Kenan Fears, U.S. Naval Research Laboratory

8:00am **BI+AS-WeM-1 Hydrophilic Polysaccharides as Building Blocks for Marine Fouling-release Coatings**, ***Axel Rosenhahn***, *V Jakobi, X Cao, W Yu, T Gnanasampanthan, R Wanka, J Schwarze, J Koc,* Ruhr-University Bochum, Germany*; M Grunze,* Heidelberg University, Germany*; J Finlay, A Clare,* Newcastle University, UK*; K Hunsucker, G Swain,* Florida Institute of Technology

Hydrophilic building blocks like polyethylene glycols are powerful ingredients in modern fouling-release coatings as they are capable to reduce the attractive hydrophobic interactions of microbes with hydrophobic matrix materials such as acrylates, silicones or polyurethanes. We explored how polysaccharides with known antiadhesive and anti-inflammatory properties in medical applications reduce the adhesion of marine fouling organisms. Among the advantages of polysaccharides is their availability, biocompatibility and degradability. Based on previous work on hydrophilic coatings [1] we focused on well hydrated hyaluronans, alginates, chitosans and chondroitin sulfate building blocks. The response of marine organisms and the ability of such components to reduce attachment and facilitate easy removal is explored on grafted monolayers of polysaccharides [2], their amphiphilic derivatives [3], and in more complex coatings such as polysaccharide containing polyelectrolyte multilayers and hybrid polymers. Lab and field experiments will be compared and discussed in the light of the previous notion that uptake of soil particles frequently challenge hydrophilic polymers when used in the real ocean environment [4].

[1] A. Rosenhahn, S. Schilp, J. Kreuzer, M. Grunze, PCCP 2010, 12, 4275

[2] X. Y. Cao, M. E. Pettit, S. L. Conlan, W. Wagner, A. D. Ho, A. S. Clare, J. A. Callow, M. E. Callow, M. Grunze, A. Rosenhahn, Biomacromol. 2009, 10, 907-915.

[3]V. Jakobi, J. Schwarze, J. A. Finlay, K. A. Nolte, S. Spöllmann, H.-W. Becker, A. S. Clare, A. Rosenhahn, Biomacromol. 2018,19, 402-408.

[4] J. Koc, T. Simovich, E. Schönemann, A. Chilkoti, H. Gardner, G.W. Swain, K. Hunsucker, A. Laschewsky, A. Rosenhahn, Biofouling 2019, DOI:10.1080/08927014.2019.1611790

8:20am **BI+AS-WeM-2 A Microfluidic Assay to Test the Adhesion of the Marine Bacterium *Cobetia Marina* Under Dynamic Shear Conditions*, Jana Schwarze*, *K Nolte, R Wanka, V Jakobi, A Rosenhahn,* Ruhr-University Bochum, Germany

Microfluidic environments with laminar flow are a useful tool to quantify attachment and removal of marine biofilm formers and cells[1–3]. We present results on the microfluidic attachment of the marine bacterium *Cobetia marina* (*C. marina*), formerly named *Halomonas marina*, as it is frequently found in marine biofilms[4,5]. To identify a suitable shear stress for the microfluidic attachment assays, the attachment behavior of *C. marina* was investigated at different shear forces on hydrophobic and hydrophilic surfaces, whereby *C. marina* tends to adhere best on hydrophobic coatings. Among the optimized assay parameters are the relevance of the growth state of *C. marina*. The optimized assay parameters will be presented as well as selected examples how coating chemistries like different self-assembling monolayers, amphiphilic alginates[6] and different thicknesses of PG coatings[7] alter the attachment of the marine bacterium *C. marina* under dynamic shear conditions.

1. Christophis, C., Grunze, M. & Rosenhahn, A. Quantification of the adhesion strength of fibroblast cells on ethylene glycol terminated self-assembled monolayers by a microfluidic shear force assay. *Phys. Chem. Chem. Phys.* (2010), 12, 4498-4504. doi:10.1039/b924304f

2. Alles, M. & Rosenhahn, A. Microfluidic detachment assay to probe the adhesion strength of diatoms. *Biofouling* (2015), 31:5, 469-480. doi:10.1080/08927014.2015.1061655

3. Nolte, K. A., Schwarze, J. & Rosenhahn, A. Microfluidic accumulation assay probes attachment of biofilm forming diatom cells. *Biofouling* (2017), 33 (7): 531-543. doi:10.1080/08927014.2017.1328058

4. Ista, L. K., Fan, H., Baca, O. & López, G. P. Attachment of bacteria to model solid surfaces' oligo(ethylene glycol) surfaces inhibit bacterial attachment. *FEMS Microbiol. Lett.* (1996), 142, 59-63. doi:10.1016/0378-1097(96)00243-1

5. Arpa-Sancet, M. P., Christophis, C. & Rosenhahn, A. Microfluidic assay to quantify the adhesion of marine bacteria. *Biointerphases* (2012), 7, 26. doi:10.1007/s13758-012-0026-x

6. Jakobi, V. *et al.* Amphiphilic Alginates for Marine Antifouling Applications. *Biomacromolecules* (2018), 19, 402-408. doi:10.1021/acs.biomac.7b01498

7. Wanka, R. *et al.* Fouling-Release Properties of Dendritic Polyglycerols against Marine Diatoms. *ACS Appl. Mater. Interfaces* (2018), 10, 34965–34973. doi:10.1021/acsami.8b12017

8:40am **BI+AS-WeM-3 Biofilm Mechanics as a Mechanism for Survival on Surfaces from Medical Device to Ship Hulls*, Paul Stoodley,*** Ohio State University **INVITED**

Bacterial biofilms are microscopic assemblages of bacterial cells usually attached to a surface and held together by a self-produced extracellular polymeric slime (EPS) matrix. Biofilms are ubiquitous in the natural environment and are highly problematic in industry and medicine where they cause corrosion, fouling, contamination and chronic medical and dental infections. The basic biology of bacterial biofilm development and strategies evolved to survive in the environment of the ancient earth are now used by the bacteria to survive on modern man-made materials. Diffusion limitation within the EPS matrix results in sharp gradients as nutrients are consumed by respiring bacteria on the periphery faster than they can diffuse in. Similarly, cell signals (molecules used to co-ordinate behavior between individual cells) and waste products, such as fermentation acids, build up in the interior of the biofilm. Biofilms are mechanically complex showing a range of behaviors from elastic solids to viscous liquids. These viscoelastic properties can facilitate survival on surfaces exposed to high shear stresses and can explain the high pressure drop and frictional losses in pipelines and ship hull fouling. However, the mechanical response may also be exploited to drive antimicrobials into the biofilm for control. The development of microenvironments combined with the structural versatility of the biofilm is the basis for the distinct biofilm phenotype as an emergent property of population of single cells and is a challenge to overcome in their control.

9:20am **BI+AS-WeM-5 Dendritic Polyglycerols as Fouling-release Coatings Against Marine Hard- and Soft Fouler*, Robin Wanka,*** Ruhr-University Bochum, Germany*; N Aldred, J Finlay,* Newcastle University, UK*; K Nolte, J Koc,* Ruhr-University Bochum, Germany*; H Gardner, K Hunsucker, G Swain,* Florida Institute of Technology*; C Anderson, A Clare,* Newcastle University, UK*; A Rosenhahn,* Ruhr-University Bochum, Germany

Polyethylene glycol (PEG) containing coatings show outstanding antifouling properties, which is commonly assigned to their hydrophilicity and their highly hydrated nature. A structurally related but hyperbranched version are polyglycerols (PGs) that increase the spatial density of non-fouling polymer units and decrease the defect density in coatings.[1,2] So far they were successfully applied in biomedicine against attachment by pathogenic bacteria. Using a surface initiated ring opening polymerization reaction[3], we grafted dendritic PGs on surfaces. The resulting samples were characterized by spectroscopic ellipsometry, contact angle goniometry, ATR-FTIR, and by degradation experiments. The prepared surfaces show excellent protein-resistance. The fouling release properties were tested in a standardized lab assay with diatoms (*Navicula incerta)* and in a dynamic field assay[4] at the FIT test site in Florida. The initial attachment of diatoms under static conditions was similar on the PGs as compared to a hydrophobic control. However, PGs show outstanding fouling release properties. Up to 94% of attached diatoms could be removed from the coatings after the exposure to a shear stress of 19 Pa. These results were confirmed in the field assays.[5] The range of testes species was also extended to macro-fouling organisms such as zoospores of green algae (*Ulva linza)* and barnacle larvae (*Balanus amphitrite*).

(1) Wyszogrodzka, M.; Haag, R. Synthesis and characterization of glycerol dendrons, self-assembled monolayers on gold: A detailed study of their protein resistance. *Biomacromolecules* **2009**, *10*, 1043–1054.

(2) Siegers, C.; Biesalski, M.; Haag, R. Self-assembled monolayers of dendritic polyglycerol derivatives on gold that resist the adsorption of proteins. *Chemistry* **2004**, *10*, 2831–2838.

(3) Weber, T.; Gies, Y.; Terfort, A. Bacteria-Repulsive Polyglycerol Surfaces by Grafting Polymerization onto Aminopropylated Surfaces. *Langmuir* **2012**, *28*, 15916–15921.

(4) Nolte, K. A.; Koc, J.; Barros, J. M.; Hunsucker, K.; Schultz, M. P.; Swain, G. E.; Rosenhahn, A. Dynamic field testing of coating chemistry candidates by a rotating disk system. *Biofouling* **2018**, *49*, 1–12.

(5) Wanka, R.; Finlay, J. A.; Nolte, K. A.; Koc, J.; Jakobi, V.; Anderson, C.; Clare, A. S.; Gardner, H.; Hunsucker, K.; Swain, G. W. *et al.* Fouling-Release Properties of Dendritic Polyglycerols against Marine Diatoms. *ACS applied materials & interfaces* **2018,** DOI: 10.1021/acsami.8b 12017 .

9:40am **BI+AS-WeM-6 Nano- and Microscale ZnO with Controllable Abundance of Surface Polarity as a Platform to Study Antibacterial Action.***, J Reeks, B Thach,* Texas Christian University*; W Moss,* Texas State University*; R Maheshwari,* Texas Academy of Mathematics and Science*; I Ali, S McGillivray, **Yuri Strzhemechny***, Texas Christian University

Nano- and microcrystalline ZnO is a low-cost, easy to synthesize material employed in many current and incipient applications owing to its exceptional optoelectronic, structural and chemical characteristics as well as a broad range of production techniques. Antibacterial action of ZnO is one of these applications, with a growing field of interdisciplinary research. Despite numerous and vigorous studies of the antibacterial nature of ZnO, and, in particular, the well- documented antimicrobial action of micro- and nanoscale ZnO particles, the most fundamental physical and chemical mechanisms driving this action are still not well identified. In particular, the influence of the crystal surface polarity on the antibacterial performance is largely unknown. Normally, hexagonal (wurtzite) ZnO crystals can be terminated with either charged polar (Zn or O) or electrically neutral nonpolar surfaces. In this work, we employ a hydrothermal growth protocol to produce ZnO nano- and microcrystals with tunable morphology, in particular to obtain a dependable control of the prevalent polarity of the free surfaces. This, in turn, can serve as a platform to investigate antibacterial action mechanisms in the synthesized specimens. It is reasonable to assume that one of the key phenomena behind such action is rooted in interactions between ZnO surfaces and the extracellular layers. Thus, excess charge or lack thereof, surface electronic charge traps, as well as variations in the stoichiometry at surfaces with different polarities of ZnO particles may affect interfacial phenomena with cell surfaces. It is possible therefore that the relative abundance of ZnO surfaces with different polarities could significantly influence their antibacterial action. In our studies, we produced ZnO crystals comparable in size with the bacteria employed in our assays, such as s. aureus. This was done intentionally in order to avoid cellular internalization of ZnO particles and thereby to address primarily the mechanisms involving ZnO/cell surface interface. These experiments were performed in conjunction with optoelectronic studies of ZnO crystals (photoluminescence, surface photovoltage) to characterize electronic structure and dominant charge transport mechanisms as fundamental phenomena governing antibacterial characteristics of our samples. We report on the results of these comparative studies relating predominant ZnO surface polarity with the antimicrobial action.

11:00am **BI+AS-WeM-10 Patterning Bacteria at Interfaces with Bio-Inspired Vascularized Polymers***, K Marquis, B Chasse,* ***Caitlin Howell,*** University of Maine

Nearly all methods of introducing bioactive compounds to the surface of a substrate rely on application from above or fail over time due to depletion. In this work, we use a bio-inspired approach to deliver target molecules to an interface from below, making use of both theoretical modeling and experimental validation to rationally design customizable patterns and gradients. Mimicking the vascular systems of living organisms, networks of empty 3D-printed channels are filled with liquid containing the compound of interest, which flows through the vascular network and diffuses through the polymer, eventually reaching the substrate surface. In proof-of-principle experiments using *Escherichia coli* and *Staphylococcus epidermidis* as model organisms, we demonstrate both theoretically and experimentally that the concentration of antibiotic and duration over which it is delivered to the surface can be controlled by varying the location of the vascular channels and concentration of the antibiotic solution inside. The result is a well-defined and predictable patterned response from the bacteria growing on the surface, a first step toward developing new types of adaptive antifouling surfaces and cell culture tools.

11:20am **BI+AS-WeM-11 Chemical Imaging of Root-Microbe Interactions***,* ***Vaithiyalingam Shutthanandan,*** *A Martinez, R Boiteau,* Pacific Northwest National Laboratory

Nutrient mobilization from soil minerals is critical for plant growth, particularly in marginal lands with high pH soils or low phosphate and iron availability. Rhizospheric bacteria enhance plant growth by converting root exudates such as sugars and amino acids into organic acids and chelating molecules that enhance mineral dissolution and improve the availability of nutrients such as phosphorous and iron. Hence, understanding the effect of iron availability on metabolite exchange between plant and micro-organism is crucial. The spatial proximity of bacteria to root tissue of specific composition and sites of root secretion is one key aspect of this exchange. In this work, the model grass Brachypodium and the bacteria Pseudomonas fluorescens are used as a model system for studying rhizosphere interactions that improve metal bioavailability. Brachypodium was grown under four different conditions such as: (1) + Fe, (2) – Fe, (3) + Pseudomonas + Fe, (4) + Pseudomonas – Fe. The plants were grown for 2 weeks in the hydroponic solution and removed from the system and the root samples were analyzed using Helium Ion Microscope (HIM) for spatial organization of bacteria within the rhizosphere of Brachypodium and X-ray photoelectron spectroscopy (XPS) for chemical imaging. HIM results clearly show bacteria colonies on the root surfaces. However, these colonies were populated preferentially within grooved structures along the surface of the root. We hypothesize that there are compositional differences in the surface of the root area that explain the presence of these 'hotspots'. Roots exposed with iron show larger bacteria colonies than the roots without iron content. XPS imaging measurements on these samples revealed four predominant compositional classes, lipids/lignin, protein, cellulose and uronic acid that were spatially resolved across the surface of the main root with ~10 ▯m resolution. Carbon and oxygen concentrations were almost constant among these samples and also constant along the individual roots. On the other hand, there is a clear variation in the concentrations of nitrogen and potassium along the root as well as among the samples. Discussion on the results and their implications will be discussed in this presentation.

11:40am **BI+AS-WeM-12 Biocompatible Silver Nanoparticles-loaded Chitosan Membranes with Antibacterial Activity Produced by Directed Liquid-Plasma Nanosynthesis***,* ***Camilo Jaramillo****, A Civantos, A Mesa, J Allain,* University of Illinois at Urbana-Champaign

Silver nanoparticles (Ag NPs) possess remarkable antibacterial properties that are widely recognized. The emergence of antibiotic-resistant bacteria has motivated the interest of Ag NPs as an alternative for antimicrobial protection, in a wide range of applications [1]. However, Ag NPs have also shown toxicity and low biocompatibility. In addition, their synthesis usually involves toxic compounds, further limiting their applicability as a biomaterial. Research on Ag NPs has largely focused on increasing their biocompatibility. Properties such as NPs size, dispersity, and stability have shown to play an important role on their biocompatibility [2]. Green synthesis methods that require non-toxic agents while giving control over these properties are of high interest.

Chitosan (CS) is a deacetylated derivative of chitin, a widely available polymer. Its properties include biodegradability, biocompatibility and non-toxicity, making it an attractive alternative for biomaterials. CS has been used as a bioactive coating (for proteins, drugs and antibiotics and as a stabilizing agent in the production of Ag NPs [3]. Approaches to synthesize CS-based Ag NPs include γ irradiation and sonochemical methods [4].

In this work, Directed Liquid-Plasma Nanosynthesis (DLPNS) was used to drive Ag NPs synthesis without the need of other reagents. CS membranes were used to immobilize the NPs, to explore their application as an antibacterial coating for biomaterials. The Ag NPs precursor concentration and irradiation time were used as control parameters. Surface topography and chemistry were studied by SEM, Contact Angle, XRD and EDS. Antimicrobial properties of the membranes were evaluated against gram-positive (*S. aureus*) and gram-negative (*E. coli*) bacteria. Life and death assays revealed the antibacterial activity of the membranes. To study their biocompatibility and cytotoxicity, mammalian cell cultures were used. Cell viability, adhesion and metabolism were evaluated via Alamar blue and immunostaining tests. SEM images were used to assess the presence of Ag NPs in the CS matrix, and observe the bacteria and cell morphology on the surface of the membranes.

[1] D. Wei, W. Sun, W. Qian, Y. Ye, X. Ma, Carbohydr. Res. 344 (2009) 2375–2382.

[2] E.I. Alarcon, M. Griffith, K.I. Udekwu, eds., Silver Nanoparticle Applications, Springer International Publishing, Cham, 2015.

[3] A. Civantos, E. Martínez-Campos, V. Ramos, C. Elvira, A. Gallardo, A. Abarrategi, ACS Biomater. Sci. Eng. 3 (2017) 1245–1261.

[4] N.M. Huang, S. Radiman, H.N. Lim, P.S. Khiew, W.S. Chiu, K.H. Lee, A. Syahida, R. Hashim, C.H. Chia, Chem. Eng. J. 155 (2009) 499–507.

12:00pm **BI+AS-WeM-13 Multifunctional 2D MoS 2 -Based Nanoplatform for Multimodal Synergistic Inactivation of Superbugs***,* ***Paresh Ray,*** Jackson State University

Development of new antibacterial therapeutic materials is becoming increasingly urgent due to the huge threat of superbugs, which are responsible for more than half of a million deaths each year in this world. We will discuss our recent report on the development of a novel nanobiomaterial based on a melittin antimicrobial peptide (AMP)-attached transition metal dichalcogenide MoS2-based theranostic nanoplatform. The reported nanoplatform has a capability for targeted identification and synergistic inactivation of 100% multidrug-resistant superbugs by a combined photo thermal therapy (PTT), photodynamic therapy (PDT), and AMP process. A novel approach for the design of a melittin antimicrobial peptide-attached MoS2-based nanoplatform is reported, which emits a very bright and photo stable fluorescence. It also generates heat as well as reactive oxygen species (ROS) in the presence of 670 nm near-infrared light, which allows it to be used as a PTT and PDT agent. Due to the presence of AMP, multifunctional AMP exhibits a significantly improved antibacterial activity for superbugs via a multimodal synergistic killing mechanism. Reported data demonstrate that nanoplatforms are capable of identification of multidrug-resistant superbugs via luminescence imaging. Experimental results show that it is possible to kill only ∼45% of superbugs via a MoS2 nanoplatform based on PTT and PDT processes together. On the other hand, killing less than 10% of superbugs is possible using melittin antimicrobial peptide alone, whereas 100% of methicillin-resistant *Staphylococcus aureus* (MRSA), drug-resistant *Escherichia coli* (*E. coli*), and drug-resistant *Klebsiella pneumoniae* (KPN) superbugs can be killed using antimicrobial peptide-attached MoS2 QDs, via a synergistic killing mechanism.

Spectroscopic Ellipsometry Focus Topic
Room A212 - Session EL+AS+EM+TF-WeM

Optical Characterization of Thin Films and Nanostructures

Moderators: Eva Bittrich, Leibniz Institute of Polymer Research Dresden, Tino Hofmann, University of North Carolina at Charlotte

8:00am **EL+AS+EM+TF-WeM-1 Enhanced Strong Near Band Edge Emission from Lanththanide Doped Sputter Deposited ZnO***, C Heng,* Beijing Institutute of Technology, China*; W Xiang, T Wang,* Beijing Institutete of Technology, China*; W Su,* Beijing Instititute of Technology, China*; P Yin,* Beihang University, China*; **Terje G Finstad,*** University of Oslo, Norway

Research on ZnO films and nanostructures have increased steadily in the last decades being motivated by many applications including photonic applications. Incorporation of rare earth (RE) elements for the purpose utilize transition therein for conversion or manipulation of the wavelength spectrum. That was also our original motivation, however we observed the REs also can provide an enhancement of near band gap emission,NBE. This has been observed for Tb, Ce, Yb and Eu. The ZnO films were co-sputtered with RE elements onto Si wafers in an $Ar+O_2$ ambient yielding oxygen rich films as observed by RBS and XPS. The films were annealed in an N_2 ambient for various temperatures from 600 to 1100 °C. The luminescence behavior was studied emission and excitation spectroscopy as well luminescence decay measurements. Both undoped and RE doped films showed a large increase in emission with increasing annealing temperature, while the increase was largest for the RE doped samples. The crystallinity and microstructure of the films were studied by XPS, SEM, XRD and HRTEM. It is observed that the increase in UV NBE is correlated with crystalline improvements of ZnO. At the temperature for maximum PL emission intensity there is silicate formation due to interaction with the substrate. The maximum occurs for an annealing temperature where not all the ZnO has been consumed in the silicate reaction. This maximum appears to be 1100 °C for the thicker films and 1000 °C for thinner films. For samples having maximum NBE there seem to be random lasing occurring indicated by the intensity dependence of UV PL emission. A hypothesis for the main reason behind the increase in NBE intensity with RE doping is that the RE ions influence the film structure during nucleation early in the deposition process by influencing the mobility of atoms. The initial grain structure will have an affect on the development grain structure for the whole film and an influence on the grain growth. This influences the presence of non-radiative defect centers in the film and the grain surface and grain boundaries. As a side effect, we observe that there is very little transfer of excitation energy to the RE ions. This supports the notion that oxygen deficient centers may be necessary to have efficient energy transfer to RE ions in ZnO. Finally we remark that strong UV light from ZnO films have been sought particularly because they could offer a low temperature production for some application. The present method is still a high temperature method, but it is very simple and can be directly combined with Si technology which can be advantage for certain applications.

8:20am **EL+AS+EM+TF-WeM-2 Ellipsometry Study of PLD based Temperature Controlled Thin Film Depositions of CdSe on ITO Substrates***, **Flavia Inbanathan,*** Ohio University*; M Ebdah,* King Saud University, Kingdom of Saudi Arabia*; P Kumar,* Gurukula Kangri Vishwavidyalaya, India*; K Dasari,* Texas State University*; R Katiyar,* University of Puerto Rico*; W Jadwisienczak,* Ohio University

Cadmium Selenide(CdSe), a n-type semiconductor with a direct bandgap of 1.73eV has been explored widely for its suitability in various applications including photovoltaics and optoelectronics, because of its optical and electrical properties. The literature presents various deposition methods for CdSe thin films out of which this work is based on pulsed laser deposition(PLD)[1]. The optoelectronic applications of CdSe thin films depend on their structural and electronic properties that depends on deposition and process parameters[2]. The stability of the thin films at various temperatures is an important factor to improve the efficiency and durability of photosensitive devices. The present work aims to fabricate the high quality CdSe thin films using PLD method and affirms the optimal deposition temperature at 250°C as validated by the films surface roughness and ellipsometry studies[3][4]. The effect of different *in-situ* deposition temperature on structural, morphological and optical properties through XRD, AFM, SEM, optical absorption/transmission and ellipsometry spectroscopy have been investigated. CdSe thin films with thickness close to 200nm were deposited on the Indium Tin Oxide (ITO) coated glass substrates at temperatures ranging from 150 to 400°C. The light absorption spectrum analysis of all the CdSe films confirmed well defined direct energy band gap from 2.03 to 1.83eV. The ITO substrate is modelled using a two sub-layers model that consists of 130nm graded ITO on top of a 0.7mm bulk ITO layer, and the experimental ellipsometry spectra agreed very well with the fitting spectra. The ellipsometry study confirmed that CdSe thin films show an increase of 44% in refractive index(*n*) in the violet spectrum, and a constant value in blue-yellow spectral range but with significant changes in red spectrum for increase in temperature upto 350°C; beyond which resulted in constant value, possibly due to the stagnation in the grain growth. The extinction coefficient(*k*) value of CdSe approaches zero in the red spectrum region for 150^{o}C and 300^{o}C temperatures whereas it showed a value of 0.25 and 0.7 for 250^{o}C and 400^{o}C temperatures, respectively. The peaks observed around 650nm and 750nm in ellipsometry spectra are assigned to excitonic transitions. The collected data will be critically analysed in terms of CdSe optical properties engineered for optoelectronic and photovoltaic applications.

References: **[1]**Z.Bao *et al.,*J.Mater.Sci.:Mater Electron(2016)27,7233-7239; **[2]**S.Mahato, *et al*., J.Scien.: Adv.Mater. Devices, (2017)2,165-171; **[3]**A.Evmenova *et al.,*Advan. Mater. Scien.Eng. (2015), ID 920421,11; **[4]**B.T.Diroll *et al*., Chem. Mater.,(2015)27,6463-6469.

8:40am **EL+AS+EM+TF-WeM-3 The Application of Mueller Matrix Spectroscopic Ellipsometry to Scatterometry Measurement of Feature Dimension and Shape for Integrated Circuit Structures***, **Alain C. Diebold,*** SUNY Polytechnic Institute **INVITED**

One of the most difficult measurement challenges is non-destructively determining the feature dimensions and shape for complicated 3D structures. This presentation will review Mueller Matrix Spectroscopic Ellipsometry based scatterometry which uses the Rigorous Coupled Wave Approximation (RCWA) to solve Maxwell's equations for a model structure and the resulting Mueller Matrix elements are compared to experimental results. Here we use the structures used in GAA transistors fabrication as an example of challenging measurements.(1, 2, 3) In this talk, we present simulations aimed at understanding the sensitivity to changes in feature shape and dimension for the structures used to fabricate GAA transistors. Simulations of the multi-layer fins show a clear sensitivity to fin shape and Si layer thickness which is enhanced by the use of the full Mueller Matrix capability vs traditional spectroscopic ellipsometry. We also discuss experimental measurement of nanowire test structure demonstrating the ability to measure the etching of mutiple sub-surface features. [3]

References

[1] Alain C. Diebold, Anthony Antonelli, and Nick Keller, Perspective: Optical measurement of feature dimensions and shapes by scatterometry, APL Mat. **6**, (2018), 058201. doi: 10.1063/1.5018310.

[2] Sonal Dey, Alain Diebold, Nick Keller, and Madhulika Korde, Mueller matrix spectroscopic ellipsometry based scatterometry simulations of Si and Si/SixGe1-x/Si/SixGe1-x/Si fins for sub-7nm node gate-all-around transistor metrology, Proc. SPIE 10585,

Metrology, Inspection, and Process Control for Microlithography XXXII, 1058506 (6 June 2018); doi: 10.1117/12.2296988

[3] Madhulika Korde, Subhadeep Kal, Cheryl Pereira, Nick Keller, Aelan Mosden, Alain C. Diebold, Optical Characterization of multi-NST Nanowire Test Structures using Muller Matrix Spectroscopic Ellipsometry (MMSE) based scatterometry for sub 5nm nodes, Proc. SPIE Metrology, Inspection, and Process Control for Microlithography XXXIII, (2019), in press.

9:20am **EL+AS+EM+TF-WeM-5 Optical Constants and Thickness of Ultrathin Thermally Evaporated Iron Films***, **Nick Allen**, D Shah, R Vanfleet, M Linford, R Davis,* Brigham Young University

Carbon nanotube templated microfabrication (CNT-M) is a technique that uses a patterned iron catalyst to grow 3-D structures for device applications. Iron catalyst thickness strongly affects carbon nanotube (CNT) growth heights and the straightness of the CNT-M structures. Atomic force microscopy has been used to directly measure the thicknesses of such iron/iron oxide films, but this technique is slow and not easily scalable. A faster method is ellipsometry, but for very thin films, the optical constants and thickness are not easily separated, thus standard ellipsometry approaches are inadequate. The 2-6 nm thick iron films used as CNT growth catalysts are in this challenging region. The absorptive nature of the iron/iron oxide films adds further difficulty. In this study, a multi-sample ellipsometry analysis using iron films of various thicknesses was performed to obtain the optical constants of thermally evaporated iron. We used contrast enhancement by incorporating a silicon dioxide layer under the film being analyzed to enhance sensitivity to the optical constants.

9:40am **EL+AS+EM+TF-WeM-6 Birefringent Photonic Crystals for Polarization-discriminatingInfrared Focal Plane Arrays*, Marc Lata,*** *Y Li, S Park, M McLamb, T Hofmann,* University of North Carolina at Charlotte

Infrared optical materials fabricated using direct laser writing have received substantial interest since the emergence

of this technology which is based on the two-photon polymerization of suitable monomers [1, 2]. We have

demonstrated that direct laser writing allows the fabrication of structured surfaces to reduce Fresnel reflection

loss in the infrared spectral range while two-dimensional photonic crystals enable optical filters with high spectral

contrast [3, 4]. In combination with the ability to fabricate large scale arrays of uniform structures, two-photon

polymerization could be a disruptive technology for enhancing focal plane arrays in IR imaging systems.

So far, photonic crystals which provide polarization selectivity have not been used for the pixel-based enhancement

of infrared focal plane arrays. Here we explore the form-birefringence found in photonic crystals composed

of arrays of subwavelength-sized slanted micro wires (Fig. 1) for this purpose. The photonic crystals investigated

here were fabricated in a single fabrication step using direct laser writing of an infrared transparent photoresist.

The lateral dimensions of the photonic crystals are comparable to the pixel size of infrared focal plane arrays which

is on the order of some tens of micrometers [5]. We observe a strong contrast under cross-polarized illumination

in the mid-infrared spectral range at w = 1550 cm-1. Finite-element-based techniques are used to optimized the

geometry of the constituents of the photonic crystals to minimize edge effects. We envision laser direct writing as

a suitable technique for the enhancement of focal plane arrays to enable focal-plane polarimeters for the infrared

spectral range.

11:00am **EL+AS+EM+TF-WeM-10 Relevance of hidden Valleys in the Dequenching of Room-temperature-emitting Ge Layers***, T Sakamoto, Y Yasutake,* University of Tokyo, Japan*; J Kanasaki,* Osaka City University, Japan*; **Susumu Fukatsu,*** University of Tokyo, Japan

Ge offers a unique advantage of gaining a deeper insight into the intervalley coupling of *hot* electrons [1], which is arguably of importance in the context of controlling the optoelectronic and photonic functionalities [2]. In view of the complicated valley degeneracy in the near-band-edge region, such intervalley coupling of electrons plays a pivotal part even when strain-engineering pseudomorphic Ge-based quantum structures.

The capability of direct-gap emission at room temperature is of considerable practical significance of Ge, for which an added advantage is that emission wavelengths fortuitously fall within the telecom bands. Moreover, Ge is particularly interesting from the device physics point of view as it outperforms many semiconductor allies in the sense that thermal *dequenching* occurs near room-temperature: the emitted light intensity increases with increasing temperature, which is convenient but nevertheless logic-defying.

Such a rather counterintuitive “thermal roll-up”, as opposed to thermal roll-off which is usually more relevant, has been interpreted in terms of two-level electron kinetics assuming local thermal equilibrium; long-lived electrons populating the indirect conduction-band bottom, i.e., L-valleys, are excited up into the direct-gap Γ-valley by absorbing phonons, which seems to fit a fairly standard phenomenological picture reasonably well. To the contrary, this model system fails in the case of Ge layers, the quality of crystallinity of which is compromised because of a low growth temperature. In fact, they only show steady thermal roll-off, viz. *quenching*, without a trace of the anticipated dequenching.

These apparently conflicting observations can be reconciled only by considering another otherwise invisible *hidden* conduction-band valley that comes in between the L andΓ valleys to decouple them. A three-level scheme is naturally invoked thereby. Indeed, it explains not only the missing dequenching but the lost local thermal equilibrium in low-quality layers. As a proof of such a conjecture, an attempt was made to directly capture the *hidden* valleys by means of time- and angle-resolved two-photon photoemission [3]. Preliminary results indicate the relevance of X(Δ)-valleys, which are slightly above the Γ-valley, in the dequenching of room-temperature emission as a result of ultrafast coupling of L-X(Δ)-Γ valleys by phonons taking up large crystal momenta. These are consistent with theory and luminescence study.

1. T. Sakamoto *et al.*, Appl. Phys. Lett. **105**, 042101 (2014).

2. Y. Yasutake and S. Fukatsu, Spoken at 2018 APS March Meeting (Los Angeles, 2018), P07.00012.

3. J . Kanasaki *et al.*, Phys. Rev. B **96**, 115301 (2017).

11:20am **EL+AS+EM+TF-WeM-11 Spectroscopic Ellipsometry on Organic Thin Films - From in-situ Bio-sensing to Active Layers for Organic Solar Cells*, Eva Bittrich*,** *P Uhlmann, K Eichhorn,* Leibniz Institute of Polymer Research Dresden, Germany*; M Schubert,* University of Nebraska-Lincoln, Linköping University, Sweden, Leibniz Institute of Polymer Research Dresden, Germany*; M Levichkova, K Walzer,* Heliatek GmbH, Germany **INVITED**

Nanostructured surfaces and thin films of small organic molecules, polymers or hybrid materials are promising interfaces for versatile applications like sensing, water purification, nanoelectronics, energy production and energy storage devices. Ellipsometry, as non-invasive method, is well suited to contribute to the understanding of structure – property – relationships in organic thin films, but can also act as probing technique for hybrid sensing elements. Aspects from our research ranging from switchable responsive polymer brush interfaces for biosensing to thin films of small organic molecules for organic solar cells will be presented. On the one hand, swelling of polymer brushes grafted to slanted columnar thin films of silicon will be visualized by anisotropic optical contrast microscopy, as an example for a new class of hybrid sensing materials with unique sensitivity on the nanoscale. On the other hand the effect of template molecules on the morphology and optical properties of semiconducting thin films will be discussed, emphasizing the correlation of ellipsometric data with structural analysis by grazing incidence wide angle X-ray scattering (GIWAXS).

12:00pm **EL+AS+EM+TF-WeM-13 Optical Dielectric Function of Si(bzimpy)2 – A Hexacoordinate Silicon Pincer Complex Determined by Spectroscopic Ellipsometry*, Yanzeng Li,*** *M Kocherga, S Park, M Lata, M McLamb, G Boreman, T Schmedake, T Hofmann,* University of North Carolina at Charlotte

Tang and VanSlyke demonstrated light emission from the first practical electroluminescent device based on a double-organic-layer structure of tris(8-hydroxyquinoline)aluminum, Alq_3, and a diamine film in the late 80's. Since then, organic light emitting diodes (OLED) based on metal chelates such as Alq3 have been widely studied. Despite the widespread use of Alq_3, there has been a broad search for new materials with improved properties, in particular, with respect to their chemical and electrochemical stability. We have recently reported on the successful synthesis of a neutral, hexacoordinate silicon-based fluorescent complex $Si(bzimpy)_2$. Our results indicate that $Si(bzimpy)_2$ exhibits inherent advantages such as the tunability of the luminescence in the visible spectrum, greater thermal stability, and high charge mobility that is comparable to that of Alq_3. Despite the successful synthesis and encouraging electroluminescence at 560 nm the complex dielectric function of the water stable complex has not been reported yet. Here we present spectroscopic ellipsometry data which were obtained from a Si(bzimpy)2 thin-film in the spectral range from 300~nm to 1900~nm. A parameterized model dielectric function composed of a Tauc-Lorentz and Gaussian oscillators is employed to analyze the experimental ellipsometry data. We find a good agreement between the critical point energies observed experimentally and our density functional theory calculations reported recently.

Electronic Materials and Photonics Division
Room A214 - Session EM+2D+AS+MI+MN+NS+TF-WeM

Nanostructures and Nanocharacterization of Electronic and Photonic Devices

Moderators: Sang M. Han, University of New Mexico, Jason Kawasaki, University of Wisconsin - Madison

8:00am **EM+2D+AS+MI+MN+NS+TF-WeM-1 Photonic Thermal Conduction in Semiconductor Nanowires***, E Tervo, M Gustafson, Z Zhang, B Cola,* ***Michael A. Filler,*** Georgia Institute of Technology

We present a practical material system—chains of infrared plasmonic resonators situated along the length of semiconductor nanowires—where near-field electromagnetic coupling between neighboring resonators enables photonic thermal transport comparable to the electronic and phononic contributions. We model the thermal conductivity of Si and InAs nanowires as a function of nanowire diameter, resonator length, aspect ratio, and separation distance by combining discrete dipolar approximation calculations, to determine the relevant dispersion relations, with thermal kinetic theory. We show that photonic thermal conductivities exceeding 1 W m^{-1} K^{-1} are possible for 10 nm diameter Si and InAs nanowires containing repeated resonators at 500 K, more than an order of magnitude higher than existing materials systems and on par with that possible with phonons and electrons. These results highlight the potential for photons in properly engineered solids to carry significant quantities of heat and suggest new ways to dynamic control thermal conductivity.

8:20am **EM+2D+AS+MI+MN+NS+TF-WeM-2 Electric Field-Induced Defect Migration and Dielectric Breakdown in ZnO Nanowires***,* ***Hantian Gao****, M Haseman,* Department of Physics, The Ohio State University*; H von Wenckstern, M Grundmann,* Universität Leipzig, Felix-Bloch-Institut für Festkörperphysik*; L Brillson,* The Ohio State University

Nanowires of the II-VI compound semiconductor ZnO have generated considerable interest for next generation opto- and microelectronics . Central to nanowire electronics is understanding and controlling native point defects, which can move[1] and lead to dielectric breakdown under applied electric fields. We used nanoscale lateral and depth-resolved cathodoluminescence spectroscopy (DRCLS) with hyperspectral imaging (HSI) in a scanning electron microscope (SEM) to observe defect migration and redistribution directly under applied electric fields and after dielectric breakdown. HSI maps represent lateral intensity distributions of specific features acquired pixel by pixel across SEM-scanned areas and normalized to near band edge (NBE) emissions. A pulsed layer deposited (PLD) ZnO microwire (3 µm diameter) exhibited homogeneous distributions of common luminescence features at 2.0 eV (V$_{Zn}$ cluster) and 2.35 eV (Cu$_{Zn}$) as well as 2.7 and 2.9 eV (V$_{Zn}$) peaks near the wire surface. With increasing electrical bias up to 3x10^5 V/cm between two Pt contacts, these defects systematically redistribute, even at room temperature, moving toward and under one of the contacts, draining the "bulk" nanowire, especially its near-surface region. Since ionized V$_{Zn}$-related and Cu$_{Zn}$ antisite defects are acceptors, their removal reduces the compensation of electron density in the typically n-type ZnO and thus its resistivity.

Besides HSI lateral maps, DRCLS vs. incident beam energy yields depth profiles radially of defects at specific locations along the nanowire. These exhibit high near-surface and wire core densities that biasing reduces. Current voltage measurements with increasing field gradients show a gradual resistivity decrease until an abrupt dielectric breakdown of the microwire at 300 kV/cm (150 V/5 µm). The acceptor removal between the contacts and their accumulation under one of the contacts can both contribute to this breakdown due to the decrease in resistivity and higher current conduction between the contacts and possible defect-assisted tunneling[2] across the increased defect density under the contact, respectively. These electric field-induced defect movements may be of more general significance in understanding dielectric breakdown mechanism not only in ZnO nanostructures but also bulk semiconductors in general.

HG, MH, and LJB gratefully acknowledge support from AFOSR Grant No. FA9550-18-1-0066 (A. Sayir). HVW and MG acknowledge Deutsche Forschungsgemeinschaft (Gr 1011/26- 1).

1. G. M. Foster, et al., Appl. Phys. Lett. **111**, 101604 (2017).

2. J.W.Cox, et al., Nano Lett, **18**, 6974 (2018).

8:40am **EM+2D+AS+MI+MN+NS+TF-WeM-3 Characterization of SiGe/Si Multilayer FIN Structures using X-Ray Diffraction Reciprocal Space Maps***,* ***Roopa Gowda****, M Korde,* SUNY Polytechnic Institute*; M Wormington,* Jordan Valley Semiconductors Inc.*; A Diebold,* SUNY Polytechnic Institute

Nanowire and Nanosheet FET's are potential replacements for FinFET's, mainly beyond sub-10nm CMOS technology nodes, as gate-all-around (GAA) FET device architecture provides improved electrostatics in higher on current (*I* on) and better subthreshold swing. As GAA is one of the best promising device for logic applications for future technology nodes, there is an increased need of characterization technique for such multilayer Si$_{1-x}$Ge$_x$/ Si complex structures. We studied Si$_{1-x}$Ge$_x$/Si/Si$_{1-}$xGex/Si/Si$_{1-x}$Ge$_x$/Simultilayer FIN structures using X-Ray Diffraction Reciprocal Space Maps (RSM). RSM is one of the most popular technique to study epitaxial thin-films nanostructures due to straightforward analysis of the data. We found RSM simulations showing sensitivity of nanosheet fin structures dimensions such as pitch-walk (PW), Nanosheet thickness (NST), composition and shape. RSM's provide better means to interpret more complex diffraction measurements than real space constructions. RSMs of Si$_{1-x}$Ge$_x$/Si multilayer structure has been simulated using Bruker JV-RADS v6.5.50/HRXRD software. 1D line profiles extracted from RSMs was also used for the analysis of nanostructures dimensions. We obtained multilayer structure dimensions from the published information. We studied the influence of nanostructure parameters PW, NST, Composition and shape on RSMs. Imperfect periodic structures impact the intensity modulation of the grating rods (GRs). We observed that satellite peaks intensity reduces and harmonics peaks intensity enhances as PW increases. Rate of intensity change in higher order peaks is much faster than the lower harmonic peaks. We observed that the spacing between adjacent interference fringes in RSMs is related to the thickness of the layers. The period of fringes is inversely proportional to the thickness of the layer, hence total FIN height can be determined. 1D line profiles along Q$_z$ shows decreased angular width and increase in intensity of the layer peak and interference fringes as NST increases. Symmetric 004 longitudinal RSMs and their line profiles clearly show layer peak shift from substrate peak as composition increases due to increase of SiGe lattice spacing along the growth direction. Cross-shaped GR pattern in RSMs is observed which is due to trapezoidal surface grating caused by SWA. Line profiles indicate that fin shapes influence the modulation of the GRs as a function of Q$_x$. We demonstrate the characterization of complex Si$_{1-x}$Ge$_x$/ Si multilayers using RSMs and their line profiles which are relevant for lateral nanowire and nanosheet FETs. Above findings from RSM simulations clearly indicate the influence of variations in structural dimensions.

9:00am **EM+2D+AS+MI+MN+NS+TF-WeM-4 Nanoscale Depth and Lithiation Dependence of V$_2$O$_5$ Band Structure by Cathodoluminescence Spectroscopy***,* ***Mitchell Walker****, N Pronin,* The Ohio State University*; A Jarry, J Ballard, G Rubloff,* University of Maryland, College Park*; L Brillson,* The Ohio State University

Vanadium pentoxide (V$_2$O$_5$) has attracted considerable interest for its potential use as a cathode for solid state lithium ion batteries. While researchers have studied the V$_2$O$_5$ lithiation charge/discharge cycle for over two decades, we are only now able to measure directly its electronic band structure from the surface to the thin film bulk and its changes with Li intercalation on a near-nanometer scale. We used depth-resolved cathodoluminescence spectroscopy (DRCLS) to monitor the changes in electronic structure from the free surface to the thin film bulk several hundred nm below. DRCLS measures optical transitions at 1.8-2, 3.1-3.2, 3.6-3.7, 4.0-4.1, and 4.6-4.7 eV between multiple conduction bands to the pristine (α) V$_2$O$_5$ valence band maximum in excellent agreement with V$_{3d}t_{2g}$ conduction band densities of states (DOS) predicted by density functional theory (DFT).[1] Triplet conduction band states at 1.8, 1.9, and 2 eV correspond to predicted V 3d$_{xy}$–O$_c$ 2p$_x$/2p$_y$ hybridized states resulting from strong deviations of the unit cell VO$_6$ octahedra from cubic coordination correspond to optical absorption edges along the 3 crystallographic axes. With excitation depth increasing from < 10 to 125 nm calibrated by Monte Carlo simulations, the relative amplitudes and energies of these states change, signifying gradual changes in octahedral distortion. The band structure changes significantly with Li intercalation into Li$_x$V$_2$O$_5$ for x = 0, 1, and 2. Lithiation gradually removes the hybridized band and introduces a 2.4-2.7 eV V$_{3d}$ t$_{2g}$ band extending 50 nm (x=1) or 25 nm (x=2) into the surface. Higher (4.0 and 4.4 eV) features possibly related to a secondary phase dominate the spectra deep inside all V$_2$O$_5$ films near the battery electrode. Delithiation reintroduces the 1.8-2 eV split-off band although significantly narrowed by octahedral distortions. Overall, DRCLS shows that the lithiation cycle alters the V$_2$O$_5$ band structure on a scale of 10-100's of nm with lithiation. The direct measure of V_2O_5's electronic band structure as a function of lithiation level provided by DRCLS can help guide future battery engineering work as more efficient lithium ion batteries are developed. In particular, these unique electrode measurements may reveal in what ways lithiation changes $V\text{-}_2O_5$ irreversibly, as well as reveal methods to extend solid state battery life. MW and LJB acknowledge support from NSF grant DMR-18-00130. AJ and GR acknowledge Nanostructures for Electrical Energy Storage (NEES), a Department of Energy Office of Science Frontier Research Center.

1. V. Eyert and K.-H. Höck, "Electronic structure of V_2O_5: Role of octahedral deformation," Phys. Rev. B 57, 12727 (1998).

9:20am **EM+2D+AS+MI+MN+NS+TF-WeM-5 Electron Microscopy of Quantum Materials: From Learning Physics to Atomic Manipulation***,* ***Sergei Kalinin,*** Oak Ridge National Laboratory **INVITED**

Atomically-resolved imaging of materials has become the mainstay of modern materials science, as enabled by advent of aberration corrected scanning transmission electron microscopy (STEM). In this talk, I will present the new opportunities enabled by physics-informed big data and machine learning technologies to extract physical information from static and dynamic STEM images. The deep learning models trained on theoretically simulated images or labeled library data demonstrate extremely high efficiency in extracting atomic coordinates and trajectories, converting massive volumes of statistical and dynamic data into structural descriptors. I further present a method to take advantage of atomic-scale observations of chemical and structural fluctuations and use them to build a generative model (including near-neghbour interactions) that can be used to predict the phase diagram of the system in a finite temperature and composition space. Similar approach is applied to probe the kinetics of solid-state reactions on a single defect level and defect formation in solids via atomic-scale observations. Finally, synergy of deep learning image analytics and real-time feedback further allows harnessing beam-induced atomic and bond dynamics to enable direct atom-by-atom fabrication. Examples of direct atomic motion over mesoscopic distances, engineered doping at selected lattice site, and assembly of multiatomic structures will be demonstrated. These advances position STEM towards transition from purely imaging tool for atomic-scale laboratory of electronic, phonon, and quantum phenomena in atomically-engineered structures.

11:00am **EM+2D+AS+MI+MN+NS+TF-WeM-10 Hot Electron Emission from Waveguide Integrated Graphene***,* ***Ragib Ahsan,*** *F Rezaeifar, H Chae, R Kapadia,* University of Southern California

From free electron laser sources to electronic structure measurements, electron emission devices play an important role in a wide range of areas. Photoemission is one of the basic processes exploited in modern electron emission devices. However, higher-order processes like multiphoton absorption or optical field induced emission are necessary for efficient photoemission from high workfunction metallic emitters. Our work demonstrates a graphene emitter integrated on a waveguide that can evanescently couple with the photons delivered from a CW laser (405 nm) and registers photoemission at a peak power that is orders of magnitude lower than previously published results based on multiphoton and optical field induced emission processes. Coupling FDTD analysis of the waveguide to a rigorous quantum mechanical study of the scattering mechanisms and the tunneling processes in graphene, we have been able to model the emission current from the graphene emitter with good agreement to the experimental data. Our investigation reveals that the photoexcited electrons can go through three mutually competitive processes: (i) electron-electron scattering (ii) electron-phonon scattering and (iii) directly emission into the vacuum. Absorption of a photon causes a reduction in the tunnel barrier seen by the electron and the emission rate increases exponentially. Integration of graphene to the waveguide enables evanescent coupling between electrons and the photons causing almost 100% absorption of the photons. Our integrated photonics approach demonstrates an emission efficiency that is three orders of magnitude greater than free space excitation. These results suggest that integrating photonic elements with low dimensional materials such as 2D materials, nanoparticles, quantum dots, etc. can provide a new domain of efficient electron emission devices and integrated photonics.

11:20am **EM+2D+AS+MI+MN+NS+TF-WeM-11 Imaging Candidate Nanoelectronic Materials with Photoemission Electron Microscopy (PEEM)***,* ***Sujitra Pookpanratana,*** *S Robey,* National Institute of Standards and Technology (NIST)*; T Ohta,* Sandia National Laboratories

The drive to produce smaller and lower power electronic components for computing is pushing the semiconductor industry to consider novel nanoscale device structures, not based solely on crystalline silicon. Continued innovation and progress towards novel nanoelectronic materials and devices in turn requires metrologies sensitive to electronic properties at these length scales. Tip-based imaging techniques provide electronic contrast with sub-nanometer resolution, however it is a local, scanning-based technique. Photoemission (or photoelectron spectroscopy) is the dominant technique to provide detailed electronic band structure information- level energies, dispersion, polarization dependence, etc. – but typically requires materials with millimeter, or larger, length scales. Photoemission electron microscopy (PEEM) can be employed to allow access to this vital information, providing full-field imaging capabilities sensitive to a variety of electronic contrast mechanisms at 10's of nanometers length scales. Here, we will present our results on imaging the impact of molecular dopants on multilayer tungsten disulfide (WS_2) employing the PEEM at the Center for Integrated Nanotechnologies within Sandia National Laboratories. We will also discuss the commissioning of a recently installed PEEM to perform complementary measurements at NIST-Gaithersburg.

Technological commercialization of transition metal dichalcogenides (TMDs) in nanoelectronics devices requires control of their electronic properties, such as charge carrier type and density, for specific device functionality. Conventional techniques for doping are problematic for atomically thin 2D materials. The sensitivity of mono- to few-layer (TMDs) to their local environment and interfaces can be employed *via* surface doping of molecules on TMDs to provide a promising route toward controllable doping. Investigations of surface doping for one to few layer WS_2 were performed using mechanically exfoliated WS_2 on a SiO_2/Si substrate that was then exposed to tris(4-bromophenyl)ammoniumyl hexachloroantimonate, a p-dopant molecule. PEEM was performed before and after p-dopant exposure. After doping, we find that the contrast of the surface WS_2 physical features change and valence band edge shifts about 0.8 eV away from the Fermi energy, consistent with p-doping. We will discuss the effects of molecular doping in terms of homogeneity and surface features across multiple WS_2 flakes. Lastly, we will discuss commissioning of a new PEEM instrument installed at NIST in 2019, using results of graphene to demonstrate imaging capability and energy resolution of this instrument.

11:40am **EM+2D+AS+MI+MN+NS+TF-WeM-12 Comparison of Features for Au and Ir Adsorbed on the Ge (110) Surface***,* ***Shirley Chiang,*** University of California, Davis*; R Xie, H Xing,* Donghua University, China*; T Rahman,* University of Central Florida*; C Fong,* University of California, Davis

Two ad-atoms of Au and Ir adsorbed, respectively, on the Ge(110) surface are studied by a first-principles algorithm based on density functional theory. The surface is modeled by a slab consisting of 108 Ge atoms with a 10 Å vacuum region. Hydrogen atoms are used to saturate the dangling orbitals at the other side of the vacuum region. Two cases of Au adsorption and one case of Ir are reported. The case of Ir has a large binding energy because of its small atomic size compared with the Ge atom, and the partially filled d-states. The total energy for each case is given, as are the energies for removing one ad-atom at a time and also both ad-atoms. The binding energy of each case is obtained by simply taking the energy difference between these configurations; this method is more realistic because the experimental data measured by LEEM and STM indicate that the collective motions of the ad-atoms do not allow the surface to relax to its equilibrium state.[1] For a large separation in the case of two Au atoms, there is a smaller binding energy than for one ad-atom. This can relate to the fact that the collective motions seen experimentally do not happen at a full monolayer coverage of ad-atoms.[1] Additional comparisons will be made to an atomic model for Ir/Ge(111) from STM measurements.[2]

[1] B. H. Stenger et al., Ultramicroscopy, 183, 72 (2017).

[2] M. van Zijll et al., Surf. Sci. 666, 90, (2017).

Support from NSF DMR-1710748 (SC, CYF); NSF DMR-1710306 (TSR); National Natural Science Foundation of China Grants 61376102, 11174048 and computational support from Shanghai Supercomputer Center (RKX, HZX).

12:00pm **EM+2D+AS+MI+MN+NS+TF-WeM-13 Reference Materials for Localization Microscopy***, C Copeland, R Dixson, L Elliott, B Ilic,* National Institute for Science and Technology (NIST)*; D Kozak, K Liao,* FDA, National Institute for Science and Technology (NIST)*; J Liddle,* NIST Center for Nanoscale Science and Technology*; A Madison,* National Institute for Science and Technology (NIST)*; J Myung,* FDA*; A Pintar,* ***Samuel Stavis****,* National Institute for Science and Technology (NIST)

As the diffraction limit fades away into the history of optical microscopy, new challenges are emerging in super-resolution measurements of diverse systems ranging from catalysts to therapeutics. In particular, due to common limitations of reference materials and microscope calibrations, many localization measurements are precise but not accurate. This can result in gross overconfidence in measurement results with statistical uncertainties that are apparently impressive but potentially meaningless, due to the unknown presence of systematic errors that are orders of magnitude larger. To solve this fundamental problem in measurement science, we are optimizing and applying nanofabrication processes to develop reference materials for localization microscopy, and demonstrating their use in quantitative methods of microscope calibration.

Our program consists of two complementary approaches. In the first, involving applied metrology, we are developing reference materials such as aperture arrays that can serve as standalone artifacts for widespread deployment. This approach will require the application of critical-dimension metrology to establish the traceability of master artifacts, and their use to calibrate a super-resolution microscope for high-throughput characterization of economical batches of reference materials. In the second approach, involving fundamental research, we are demonstrating the application of reference materials and calibration methods in our own experimental measurements. Most interestingly, achieving vertical integration of our two approaches and the unique capabilities that result, we are building reference materials into measurement devices for in situ calibration of localization measurements for nanoparticle characterization.

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New Challenges to Reproducible Data and Analysis Focus Topic
Room A124-125 - Session RA+AS+CA+PS+TF-WeM
Reproducibility in Science and Engineering, including materials and energy systems

Moderators: Karen Gaskell, University of Maryland, College Park, Svitlana Pylypenko, Colorado School of Mines

8:00am **RA+AS+CA+PS+TF-WeM-1 Reproducibility and Replicability in Science and Engineering: a Report by the National Academies***, T Winters,* National Academies of Sciences, Engineering, and Medicine*;* ***Dianne Chong****,* Boeing Research and Technology (Retired) **INVITED**

One of the pathways by which scientists confirm the validity of a new finding or discovery is by repeating the research that produced it. When a scientific effort fails to independently confirm the computations or results of a previous study, some argue that the observed inconsistency may be an important precursor to new discovery while others fear it may be a symptom of a lack of rigor in science. When a newly reported scientific study has far-reaching implications for science or a major, potential impact on the public, the question of its reliability takes on heightened importance. Concerns over reproducibility and replicability have been expressed in both scientific and popular media.

As these concerns increased in recent years, Congress directed the National Science Foundation to contract with the National Academies of Science, Engineering, and Medicine to undertake a study to assess reproducibility and replicability in scientific and engineering research and to provide findings and recommendations for improving rigor and transparency in research.

The committee appointed by the National Academies to carry out this task included individuals representing a wide range of expertise: methodology and statistics, philosophy of science, science communication, behavioral and social sciences, earth and life sciences, physical sciences, computational science, engineering, academic leadership, journal editors, and industry expertise in quality control. Individuals with expertise pertaining to reproducibility and replicability of research results across a variety of fields were included as well.

This presentation will discuss the committee's approach to the task and its findings, conclusions, and recommendations related to factors that influence reproducibility, sources of replicability, strategies for supporting reproducibility and replicability, and how reproducibility and replicability fit into the broader framework of scientific quality and rigor.

8:40am **RA+AS+CA+PS+TF-WeM-3 Directly Assessing Reproducibility in Materials Chemistry Research Using Literature Meta-analysis***,* ***David Sholl****,* Georgia Institute of Technology **INVITED**

While it is widely agreed that making reported research more reproducible is a desirable goal, less is known about how reproducible current work in materials chemistry is. I will discuss using literature meta-analysis as a tool to obtain quantitative insight into the reproducibility of materials chemistry experiments. Case studies will be discussed involving measurements of gas adsorption in metal-organic frameworks and the synthesis of metal-organic framework materials. These are useful examples to study because comprehensive databases of information from the open literature are available, but they share features that are common in many areas of material chemistry. Insights from these case studies suggest possible paths towards improving data reproducibility for individual researchers, for academic departments and for professional organizations.

9:20am **RA+AS+CA+PS+TF-WeM-5 Reproducibility in Fundamental and Applied Science***,* ***George Crabtree****,* Argonne National Laboratory, University of Illinois at Chicago **INVITED**

The scientific enterprise operates via a few basic features, including questions, insight, hypotheses, critique, reproducibility, elaboration and revision. All contribute to the process of discovery, none can be taken as the single signature of scientific truth. Discovery science is a dynamic process informed by new observations and continuous refinement of the precision, accuracy, principals and scope of our collective scientific knowledge. History has many examples of significant revisions of previously accepted dogma based on new observations (the earth is flat, matter is infinitely divisible, the stars are fixed). New insights lead to new fundamental principles (energy is conserved, nothing can go faster than light, germs cause disease) that open new opportunities for advancing the scientific frontier and raising the quality of life. Examples of advances of the frontiers of energy science and their implications for reproducibility will be given.

11:00am **RA+AS+CA+PS+TF-WeM-10 Representativeness of a TEM image for Revealing New Phenomenon in Energy Storage Materials***,* ***Chongmin Wang****,* Pacific Norththwest National Laboratory*; D Baer,* Pacific Northwest National Laboratory

Transmission electron microscopy (TEM), as a imaging technique with high spatial resolution, appears to be a routine tool for showcasing, often viewed as an enlightening figure, the structural and chemical information of materials at multiscale of down to single atomic column. One of a very common questions that raised by the viewer, not necessarily suspicious, is the representativeness of the image to the real situation as considering the sampling scale of the TEM imaging method. This question is further elevated for the case of in-situ and operando observation as which naturally couples in another dimension of “time” in addition to the “spatial” scale. In addition, beam effect can be coupled in for artifacts. In this presentation, we will check into the reproducibility of TEM imaging of both in-situ and ex-situ for revealing new phenomenon in energy storage materials, while certain cautions may also be necessary for interpreting new observations based on TEM.

11:20am **RA+AS+CA+PS+TF-WeM-11 Reproducibility Issues when Developing Catalysts for Fuel Cell Applications***, M Dzara, S Zaccarine,* Colorado School of Mines*; K Artyushkova,* Physical Electronics and University of New Mexico*;* ***Svitlana Pylypenko****,* Colorado School of Mines

This talk will discuss reproducibility issues encountered during the development of novel catalysts for low temperature fuel cell performance (PEMFC) as replacements of state-of-the-art catalysts that contain Pt-based nanoparticles supported on a high surface area carbon support. Examples across several catalytic systems will be shown, including low platinum-group metal (low-PGM) catalysts with extended surfaces derived from nanowire templates, and PGM-free catalysts based on N-doped carbon with an atomically dispersed transition metal.

Reproducibility issues related to the synthesis of these catalytic materials and their impact on the performance of these catalysts will be reported first following by discussion of challenges in characterization. Specifically, the need for complementary characterization will be highlighted along with issues that arise when materials are characterized by different groups using different techniques. Another set of reproducibility issues arises when conducting characterization of catalysts under in-situ and in-operando conditions.[1] The time constraints imposed by the availability of instrumentation result in datasets that have a limited number of samples, areas per samples and replicate measurements on the same sample.

(1) Dzara, M. J.; Artyushkova, K.; Shulda, S.; Strand, M. B.; Ngo, C.; Crumlin, E. J.; Gennett, T.; Pylypenko, S. Characterization of Complex Interactions at the Gas − Solid Interface with in Situ Spectroscopy : The Case of Nitrogen-Functionalized Carbon. *J. Phys. Chem. C***2019**, *123* (14), 9074–9086.

11:40am **RA+AS+CA+PS+TF-WeM-12 Challenges in Multimodal Spectroscopic Analysis of Energy Storage Materials***, **Vijayakumar Murugesan,*** Pacific Norththwest National Laboratory*; K Mueller,* Joint Center for Energy Storage Research (JCESR) **INVITED**

Charge transfer across heterogeneous interfaces facilitated by redox reactions is the basis of energy storage technology. Capturing the interfacial processes over broad scales both spatially (ranging from angstroms up to 100 nm) and temporally (lasting from fs up to a few minutes) is a major challenge. This is one origin of the existing knowledge gaps in energy storage materials, which impede our ability to predict and control the emergent behaviors at electrochemical interfaces. As part of Joint Center for Energy Storage Research (JCESR) center, we developed a multi-modal in situ characterization tool set based on X-ray absorption, photoelectron and multinuclear NMR spectroscopy in combination with computational modelling that can access a range of the important complex processes. This multimodal approach helps us gain critical insights of the charge transfer process, but also presented unique challenges in data collection, analysis and reproducibility. The multitude of constituents and varying surface chemistry combined with external stimuli (applied potential and temperature) challenges the traditionally conceived time and spatial resolution limitations of the probes. For example, establishing reference systems and base line measurements for electrochemical process where combinatorial constituents react and depend on the charge state is a major challenge in spectroscopic studies and complicates subsequent corroboration with computational analysis. In this talk, we will discuss overcoming these challenges and apply the methods to critically analyzing solid-electrolyte interphase (SEI) evolution in Li-metal based batteries, multivalent ion transport across membranes and chemical stability of redox flow battery electrolytes.

Applied Surface Science Division
Room A211 - Session AS+CA+LS-WeA

Operando Characterization Techniques for In situ Surface Analysis of Energy Devices

Moderator: Svitlana Pylypenko, Colorado School of Mines

2:20pm **AS+CA+LS-WeA-1 Probing the Electronic Structure of Electrocatalysts and the Formation of Reaction Intermediates*, Kelsey Stoerzinger,*** Oregon State University **INVITED**

Electrocatalysts are important constituents in numerous energy conversion and storage processes. Reactants adsorb onto the electrocatalyst surface, where the interplay of electronic states results in a lower activation barrier for the transfer of electronic and ionic species in the reaction pathway to product formation. Rational design of electrocatalysts with greater activity for higher efficiency devices requires an understanding of the material's electronic structure in situ, as well as the reaction intermediates involved.

Many surface science techniques, such as X-ray photoelectron spectroscopy (XPS), collect information from inherently surface-sensitive low-energy processes, requiring operation in ultrahigh vacuum. This constraint is lifted for ambient pressure XPS, which can probe the surface in equilibrium with the gas phase at pressures up to ~a few Torr, or with thin liquid layers using a higher incident photon energy. This presentation will discuss the insights obtained with this technique regarding the electronic structure of oxide electrocatalysts in an oxidizing or humid environment, as well as the reaction intermediates of relevance to electrocatalysis.[1] I will then extend the technique to probe electrocatalysts *in operando*,[2] driving current through a thin layer of liquid electrolyte and employing a tender X-ray source.

References:

[1] Stoerzinger,K.A.Wang, L. Ye, Y. Bowden, M. Crumlin, E.J. Du, Y. Chambers, S.A. "Linking surface chemistry to photovoltage in Sr-substituted $LaFeO_3$ for water oxidation". *Journal of Materials Chemistry A* 6 (2018) 22170-22178.

[2] Stoerzinger, K.A. Wang, X.R. Hwang, J. Rao, R.R Hong, W.T Rouleau, C.M. Lee, D. Yu, Y. Crumlin, E.J. Shao-Horn, Y. "Speciation and electronic structure of $La_{1-x}Sr_xCoO_{3-\delta}$ during oxygen electrolysis". *Topics in Catalysis* 61 (2018) 2161–2174.

3:00pm **AS+CA+LS-WeA-3 Surface Characterization of Battery Electrode/Electrolyte Materials Using XPS and ToF-SIMS*, Elisa Harrison,*** *S Peczonczyk, S Simko,* Ford Motor Company*; K Wujcik,* Blue Current*; A Sharafi, A Drews,* Ford Motor Company

With a drive to develop hybrid electric and electric vehicles for improving fuel economy and lowering emissions, research of battery materials becomes necessary to increase the performance and durability of automotive batteries. Therefore, significant improvements in the energy capacity, stability, and safety of automotive batteries must be achieved. For the last two decades, traditional methods to characterize battery materials and interfaces have focused on the mechanical and electrochemical properties of the battery. There has been less emphasis on understanding chemical properties of the surface of the electrode and the chemistry that occurs at the electrode/electrolyte interface. Moving forward to develop new battery systems, gaining an understanding of the surface chemistry of battery materials is critical to improving performance.

The objective of this work is to highlight the need for surface analytical techniques and methodologies to fully characterize and improve battery materials. In this work, the surface chemistry of electrodes and electrolytes were analyzed using both X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). These are powerful tools to identify slight changes to the surface chemistry of battery materials with respect to factors such as electrode and electrolyte formulation, cycling conditions, air exposure, contamination, and sample replication.

3:20pm **AS+CA+LS-WeA-4 In Operando Molecular Imaging of Microbes as an Electrode*, Xiao-Ying Yu,*** Pacific Northwest National Laboratory

Metal reducing bacteria, such as *Shewanella* and *Geobacter*, has attracted attention in recent years particularly for the potential as Genome Encoded Materials. They also can function as electrodes in microbial fuel cells (MFCs). Despite the surging interest and applications of various imaging tools to understand the microbial populations, little has been explored in the *in vivo* study of MFCs using novel *in operando* electrochemical spectroscopy. We have invented a System for Analysis at the Liquid Vacuum Interface (SALVI) microfluidic cell that is suitable for culturing bacterial biofilms for *in vivo* molecular imaging. We have also illustrated that the electrochemical verison of SALVI or the E-cell is viable for *in operando* study of the electrode-electrolyte interface. We have cultured *Shewanella* and *Geobacter sulfurreducens* biofilms in SALVI and published several papers recently. In this presentation, I will show most recent *in operando* molecular imaging results using E-cell and *in situ* liquid SIMS to investigate electron transport using *Shewanella* as a model MFC electrode.

4:20pm **AS+CA+LS-WeA-7 Operando-XPS Investigation of Low-Volatile Liquids and Their Interfaces using Lab-Based Instruments*, Sefik Suzer,*** Bilkent University, Turkey **INVITED**

X-Ray based Operando Investigations have traditionally been carried out in Synchrotron facilities, due to demanding instrumentation and expertise.[1, 2] However, although sporadic, several important lab-based XPS studies have also been reported.[3] Emergence of Ionic Liquids with several promising properties, including their low volatility, has rekindled the use of XPS, especially for Operando types of measurements.[4] Our initial investigations had also concentrated on ionic-liquids and their interfaces under **dc** and **ac** electrical bias, and extended to monitoring electrochemical reactions.[5, 6] Recently, we have been investigating other low-volatile liquids and their drops on various substrates to tap into the Electrowetting phenomena.[7, 8] The common theme in all of our studies is the use of bias dependent shifts in the positions of the core-levels as reflection of the electrical potentials, recorded in a totally non-invasive and chemically resolved fashion. We use the magnitude and the frequency dependence of such potentials to extract pertinent information related to chemical and/or electrochemical properties of the materials and their interfaces. Several examples using ionic liquids, liquid poly-ethylene-glycol (PEG) and their mixtures will be presented and discussed.

References:

[1] Bluhm, H.; Andersson, K.; Araki, T.; Benzerara, K.; Brown, G. E.; Dynes, J. J.; Ghosal, S.; Gilles, M. K.; Hansen, H.-C.; Hemminger, J., J. Electron Spectrosc. Relat. Phenom. **150**, 86-104 (2006).

[2] Lichterman, M. F., Hu, S., Richter, M. H., Crumlin, E. J., Axnanda, S., Favaro, M., Drisdell, W., Hussain, Z., Mayer, T., Brunschwig, B. S., Lewis, N. S., Liu, Z. & Lewerenz, H.-J. Energy & Environmental Science **8**, 2409-2416 (2015).

[3] Foelske-Schmitz; A., Ruch; P.W., Kötz; R., J. Electron Spectrosc. Relat. Phenom. **182**, 57-62 (2010).

[4] Lovelock, K. R. J., Villar-Garcia, I. J., Maier, F., Steinrück, H.-P. & Licence, P.. Chemical Reviews **110**, 5158-5190, (2010).

[5] Camci, M.; Aydogan, P.; Ulgut, B.; Kocabas, C.; Suzer, S., Phys. Chem. Chem. Phys. **8**, 28434-28440 (2016).

[6] Camci, M. T.; Ulgut, B.; Kocabas, C.; Suzer, S., ACS Omega **2**, 478-486 (2017).

[7] Gokturk; P.A., Ulgut; B., Suzer; S., Langmuir **34**, 7301-7308 (2018).

[8] Gokturk; P.A., Ulgut; B., Suzer; S., Langmuir **35**, 3319-3326 (2019).

5:00pm **AS+CA+LS-WeA-9 Decoupling Surface and Interface Evolution in Polymer Electrolyte Membrane Systems Through In Situ X-Ray Photoelectron Spectroscopy*, Michael Dzara*[1][2]*,*** Colorado School of Mines*; K Artyushkova,* Physical Electronics*; H Eskandari, K Karan,* University of Calgary, Canada*; K Neyerlin,* National Renewable Energy Laboratory*; S Pylypenko,* Colorado School of Mines

Ambient pressure X-ray photoelectron spectroscopy (AP-XPS) enables surface sensitive study of gas-solid interfaces. The fundamental knowledge obtained from such measurements provides unparalleled insight into the physicochemical processes that drive electrocatalytic devices.[1] Studies featuring AP-XPS span a broad range of materials and reactions, with many focused on thin films or other well-defined materials. In such studies, there are often clear changes in the material upon transition from ultra-high vacuum to *in situ* conditions, or there are well-defined catalyst species that participate in the relevant process.

In this work, the differing evolution of the many interfaces in polymer electrolyte membrane (PEM) electrodes in the presence of water vapor is studied through detailed analysis of AP-XP spectra. The complexity of analyzing these interfaces arises from the presence of both catalyst and

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[1] **ASSD Student Award Finalist**

[2] **National Student Award Finalist**

ionomer species in PEM electrodes, and the subtlety of the changes induced in AP-XP spectra by interactions between the catalyst, ionomer, and gas. Adsorption of a gaseous reactant species onto a catalyst's surface results in a weak interaction and a small chemical shift in the adsorbent species, while ionomer may undergo re-orientation or degradation upon exposure to reactants, also altering the spectra. Therefore, spectral subtraction and highly-constrained curve fitting are applied to enable reliable identification of catalyst adsorbing sites and adsorption/desorption trends,[2] and ionomer changes in the presence of water vapor. Interactions between platinum-group metal-based catalysts and ionomer films with water vapor are first studied independently, and then simultaneously at the electrode scale. Such an approach allows changes in the electrode-water interface to be decoupled and assigned to either catalyst adsorption behavior, or ionomer response. This work lays the foundation for future study of different classes of electrocatalysts at the electrode scale, and *in operando* AP-XPS studies of electrocatalytic processes.

(1) Starr, D. E.; Liu, Z.; Hävecker, M.; Knop-Gericke, A.; Bluhm, H. Investigation of Solid/Vapor Interfaces Using Ambient Pressure X-Ray Photoelectron Spectroscopy. *Chem. Soc. Rev.***2013**, *42*, 5833–5857.

(2) Dzara, M. J.; Artyushkova, K.; Shulda, S.; Strand, M. B.; Ngo, C.; Crumlin, E. J.; Gennett, T.; Pylypenko, S. Characterization of Complex Interactions at the Gas − Solid Interface with in Situ Spectroscopy : The Case of Nitrogen-Functionalized Carbon. *J. Phys. Chem. C***2019**, *123* (14), 9074–9086.

5:20pm **AS+CA+LS-WeA-10 Low Temperature Scanning Tunneling Microscopy and Spectroscopy of Semiconductor Nanowire Device Surfaces***, **Yen-Po Liu**, Y Liu, S Mousavi, L Sodergren, F Lindelöw, S Lehmann, K Dick Thelander, E Lind, R Timm, A Mikkelsen,* Lund University, Sweden

III-V semiconductor nanowires (NWs) show considerable promise as components in efficient and fast electronics as well as for quantum computing. In particular, the surfaces of the NWs play a significant role in their function due to the large surface to bulk ratio. Further, as the incorporation and activation of the nanowires in a device can affect their structure, it is relevant to study the surface structure and its influence on electronic properties in devices and during operation.

We use atomically resolved Scanning Tunneling Microscopy/Spectroscopy (STM/S) to study InAs and GaAs NWs in planar device configurations. [1-3] We use atomic hydrogen cleaning at 400°C to obtain well-defined surfaces that can be scanned with STM while the complete device is still fully functioning. [2] We study both NWs grown directly in a planar configuration as well as wires harvested from a growth substrate and placed on top of predefined metal contacts with ~100nm precision using a micro/nano probe. In our new <10K closed-cycle STM we can identify the individual device NWs simultaneously as we can apply voltages across the devices using four additional electrical contacts in the low temperature STM. We initially investigate NW device geometric structure and morphology with high precision. Then we continue to perform atomic resolution and low temperature STS mapping on top of the NWs surfaces to investigate electronic structure and potential quantum confinement effects as well as the influence of defects. These measurements can be performed while the device is actively operating by external biases applied and the I(V) characteristic across the NW is obtained. The STM tip can also act as a role as a local gate for Scanning Gate Microscopy (SGM) [4], which we can precisely locate on the operating single NWs device for SGM on the areas as STM is performed.

[1] Persson, O. et al., (2015). *Nano Letters*, 15(6), pp.3684-3691.

[2] Webb, J. et al., (2017). *Scientific Reports* 7, 12790

[3] Hjort, M. et al., (2015). *ACS Nano*, 8(12), pp.12346-12355

[4] Webb J.L. et al., (2014). Nano Research 7, 877

5:40pm **AS+CA+LS-WeA-11 Work-function Estimation and In situ Measurement of Photoemission Spectroscopy of $CuFeO_2$ under Near Ambient Condition***, **Soumya Banerjee**, P Sapkota,* University of Notre Dame*; A Cabrera,* Pontificia Universidad Católica de Chile, Chile*; S Ptasinska,* University of Notre Dame

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 H2O 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. The work functions of pure and Ga-doped Delafossite p-type $CuFeO_2$ semiconductor crystals with different thicknesses were measured using near ambient pressure x-ray photoemission spectroscopy (NAP-XPS) in Ar ambient. The values differ with changing thickness as well as Ga doping. The effect of water and CO_2 on the samples was also studied using NAP-XPS to understand the interaction between atmospheric gases and $CuFeO_2$ which may be helpful for its practical application in solar cells. No significant changes were found in XPS result obtained from $CuFeO_2$ in water ambient with and without illumination whereas CO_2 induced changes in oxygen XPS peak positions.

6:00pm **AS+CA+LS-WeA-12 In-situ X-ray Photoelectron Spectroscopic Study of III-V Semiconductor/H_2O Interfaces under Light Illumination***, **Pitambar Sapkota**, S Ptasinska,* University of Notre Dame

A number of studies on different semiconductor materials that can be used as a photoelectrode in photoelectron-chemical (PEC) cells for solar water splitting is continually growing in material sciences and solar energy communities. III-V based compounds have been the most promising candidates because of their efficient light and carrier management properties in addition to suitable band gap and band edge energies, which properly match the solar spectrum and water redox potentials, respectively. Although most of the highly efficient PEC water splitting cells are based on III-V semiconductor, these photoelectrode materials are unstable under operational conditions. Few studies suggest oxidation leading to corrosion as a major cause of the degradation of these photoelectrodes, but it is still not completely understood and little is known about the role of the oxides formed at the interfaces. Therefore, knowledge of the interfacial reactions in realistic situations and surface dynamics are necessary to advance our understanding of water splitting mechanism, as well as to build a stable and efficient PEC solar water splitting cell. In this study, we used state of the art spectroscopic technique, ambient pressure X-ray photoelectron spectroscopy, to characterize semiconductor (GaAs and GaP) surface and to study chemical reactions occurring at the water interface in presence of secondary light source. Core level photoemission spectra from Ga2p, As3d, P2p, and O1s were collected at different water pressures in presence of secondary light source to identify the newly formed surface species, particularly oxides, and to evaluate the interaction of GaAs and GaP with water under light illumination.

This research is based upon work supported by the U.S. Department of Energy Office of Science, Office of Basic Energy Sciences under Award Number DE-FC02-04ER15533.

Advanced Ion Microscopy and Ion Beam Nano-engineering Focus Topic

Room B231-232 - Session HI+AS+CA-WeA

Advanced Ion Microscopy and Surface Analysis Applications

Moderators: Richard Livengood, Intel Corporation, Armin Gölzhäuser, University of Bielefeld, Germany

2:20pm **HI+AS+CA-WeA-1 Analytical Capabilities on FIB Instruments using SIMS: Applications, Current Developments and Prospects***, **Tom Wirtz**,* Luxembourg Institute of Science and Technology, Luxembourg*; J Audinot,* Luxembourg Institute of Science and Technology, Luxembourg*; J Lovric, O De Castro,* Luxembourg Institute of Science and Technology, Luxembourg **INVITED**

Secondary Ion Mass Spectrometry (SIMS) is an extremely powerful technique for analyzing surfaces, owing in particular to its ability to detect all elements from H to U and to differentiate between isotopes, its excellent sensitivity and its high dynamic range. SIMS analyses can be performed in different analysis modes: acquisition of mass spectra, depth profiling, 2D and 3D imaging. Adding SIMS capability to FIB instruments offers a number of interesting possibilities, including highly sensitive analytics, in-situ process control during patterning and milling, highest resolution SIMS imaging (~10 nm), and direct correlation of SIMS data with data obtained with other analytical or imaging techniques on the same instrument, such as high resolution SE images or EDS spectra [1,2].

Past attempts of performing SIMS on FIB instruments were rather unsuccessful due to unattractive detection limits, which were due to (i) low ionization yields of sputtered particles, (ii) extraction optics with limited collection efficiency of secondary ions and (iii) mass spectrometers having low duty cycles and/or low transmission. In order to overcome these limitations, we have investigated the use of different primary ion species and of reactive gas flooding during FIB-SIMS and we have developed compact high-performance magnetic sector mass spectrometers operating in the DC mode with dedicated high-efficiency extraction optics. We installed such SIMS systems on different FIB based instruments, including the Helium Ion Microscope [3-5], a FIB-SEM DualBeam instrument and the npSCOPE instrument, which is an integrated Gas Field Ion Source enabled instrument combining SE, SIMS and STIM imaging with capabilities to analyse the sample under cryo-conditions.

Here, we will review the performance of the different instruments with a focus on new developments such as cryo-capabilities and new detectors allowing parallel detection of all masses, present a number of examples from various fields of applications (nanoparticles, battery materials, photovoltaics, micro-electronics, tissue and sub-cellular imaging in biology, geology,…) and give an outlook on new trends and prospects.

[1] T. Wirtz, P. Philipp, J.-N. Audinot, D. Dowsett, S. Eswara, Nanotechnology 26 (2015) 434001

[2] F. Vollnhals, J.-N. Audinot, T. Wirtz, M. Mercier-Bonin, I. Fourquaux, B. Schroeppel, U. Kraushaar, V. Lev-Ram, M. H. Ellisman, S. Eswara, Anal. Chem. 89 (2017) 10702

[3] D. Dowsett, T. Wirtz, Anal. Chem. 89 (2017) 8957

[4] T. Wirtz, D. Dowsett, P. Philipp, Helium Ion Microscopy, ed. by G. Hlawacek, A. Gölzhäuser, Springer, 2017

[5] T. Wirtz, O. De Castro, J.-N. Audinot, P. Philipp, Ann. Rev. Anal. Chem. 12 (2019)

3:00pm **HI+AS+CA-WeA-3 Correlated Materials Characterization via Multimodal Chemical Imaging using HIM-SIMS**, *A Belianinov,* Oak Ridge National Laboratory*; S Kim,* Pusan National University, South Korea*; A Trofimov,* ***Olga S. Ovchinnikova,*** Oak Ridge National Laboratory

Multimodal chemical imaging simultaneously offers high resolution chemical and physical information with nanoscale, and in select cases atomic, resolution. By coupling modalities that collect physical and chemical information, we can address a new set of scientific problems in biological systems, battery and fuel cell research, catalysis, pharmaceuticals, photovoltaics, medicine and many others. The combined multimodal platforms enable local correlation of material properties with chemical makeup, making fundamental questions in how chemistry and structure drive functionality approachable. The goal of multimodal imaging is to transcend the existing analytical capabilities for nanometer scale spatially resolved material characterization at interfaces through a unique merger of advanced microscopy, mass spectrometry and optical spectroscopy.Combining helium ion microscopy (HIM) and secondary ion mass spectrometry (SIMS) onto one platform has been demonstrated as a method for high resolution spot sampling and imaging of substrates. To advance this approach and to expand its capabilities I will present our results of multimodal chemical imaging using this technique on test substrates and show application of this approach for the multimodal analysis of perovskite (HOIPs) materials. I will discuss the performance metrics of the multimodal imaging system on conductive and non-conductive materials and discuss our results on understanding the chemical nature of ferroelastics twin domains in methylammonium lead triiodide (MAPbI3) perovskite using HIM-SIMS.

3:20pm **HI+AS+CA-WeA-4 Compositional Characterization of Biogenic Nanoparticles using the ORION NanoFab with SIMS**, ***Christelle Guillermier,*** *F Khanom,* Carl Zeiss PCS, Inc.*; D Medina,* Northeastern University*; J Audinot,* Luxembourg Institute of Science and Technology, Luxembourg

Over the past several years, the use of both nanoparticles and nanostructured surfaces have emerged as an alternative's solution to antibiotic resistant bacteria as they effectively decrease bacterial survival without being highly toxic to mammalian cells. These nanoparticles whose sizes span 10 nm to several hundred nm are composed of a variety of materials such as pure metals, metal oxides, and metalloids. Their chemical characterization however remains a challenge due to their small sizes. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) are the conventional analytical techniques of choice to determine the nanoparticles' morphology, size, and elemental composition. However, although sensitive enough to detect trace elements, SEM and EDX cannot provide elemental information for the smallest features on a bulk sample, or for the lightest elements.

The ORION NanoFab is an ion microscope that allows for high resolution secondary electron (SE) imaging with a He^+ focused ion beam that can be focused to a 0.5 nm probe size. The same instrument offers a Ne^+ ion beam with a focused probe size of 2 nm. Recently, this same platform has been configured with a custom-designed magnetic sector secondary ion mass spectrometer (SIMS). It allows for the detection of all periodic table elements including H and Li which EDS cannot easily detect. Importantly, SIMS with neon provides elemental imaging with spatial resolution smaller than 20 nm. The combination of high resolution He^+ imaging (0.5 nm) with Ne^+ SIMS elemental mapping yields a direct correlative technique particularly attractive for exploring nanoparticles and nanofeatures in general.

NanoFab-SIMS has already yielded information-rich images in diverse fields of applications. We will here illustrate its potential for the characterization of biogenic nanoparticles made by bacteria and plants.

4:20pm **HI+AS+CA-WeA-7 Effects of Ion Irradiation on Two-Dimensional Targets: What is Different from Bulk Materials**, ***Arkady V. Krasheninnikov,*** Helmholtz-Zentrum Dresden-Rossendorf, Germany **INVITED**

Ion irradiation has successfully been used for introducing impurities and creating defects in two-dimensional (2D) materials in a controllable manner. Moreover, focused ion beams, especially when combined with in-situ or post-irradiation chemical treatments, can be employed for patterning and even cutting 2D systems with a high spatial resolution. The optimization of this process requires the complete microscopic understanding of the interaction of energetic ions with the low-dimensional targets.

In my presentation, I will dwell upon the multi-scale atomistic computer simulations of the impacts of ions onto free-standing (e.g., suspended on a TEM grid) and supported (deposited on various substrates) 2D materials, including graphene and transition metal dichalcogenides (TMDs), such as MoS2 and WS2. I will emphasize the differences between defect production under ion irradiation in 2D materials and bulk solids. The theoretical results will be augmented by the experimental data obtained by the coworkers. I will further present the results of multi-scale simulations of ion irradiation of free-standing [1] and supported [2] graphene and 2D TMDs, and demonstrate that depending on ion mass and energy, the defect production can be dominated by direct ion impacts, back scattered ions or atoms sputtered from the substrate [2]. Finally, I will touch upon the interaction of highly-charged [3] and swift heavy ions [4] with 2D systems and overview recent progress in modelling this using non-adiabatic approaches including time-dependent density functional theory and Ehrenfest dynamics [5].

1. M. Ghorbani-Asl, S. Kretschmer, D.E. Spearot, and A. V. Krasheninnikov, 2D Materials 4 (2017) 025078.

2. S. Kretschmer, M. Maslov, S. Ghaderzadeh, M. Ghorbani-Asl, G. Hlawacek, and A. V. Krasheninnikov, ACS Applied Materials & Interfaces 10 (2018) 30827.

3. R. A. Wilhelm, E. Gruber, J. Schwestka, R. Kozubek, T.I. Madeira, J.P. Marques, J. Kobus, A. V. Krasheninnikov, M. Schleberger, and F. Aumayr, Phys. Rev. Lett. 119 (2017) 103401.

4. R. Kozubek, M. Tripathi, M. Ghorbani-Asl, S. Kretschmer, L. Madauß, E. Pollmann, M. O'Brien, N. McEvoy, U. Ludacka, T. Susi, G.S. Duesberg, R.A. Wilhelm, A. V. Krasheninnikov, J. Kotakoski, and M. Schleberger J. Phys. Chem. Lett. 10 (2019) 904.

5. A. Ojanperä, A. V. Krasheninnikov, and M. Puska, Phys. Rev. B 89 (2014) 035120.

5:00pm **HI+AS+CA-WeA-9 Effects of He Ion Irradiation on Gold Nanoclusters: a Molecular Dynamics Study**, ***Sadegh Ghaderzadeh,*** *M Ghorbani-Asl, S Kretschmer, G Hlawacek,* Helmholtz-Zentrum Dresden Rossendorf, Germany*; A Krasheninnikov,* Helmholtz-Zentrum Dresden-Rossendorf, Germany

The interpretation of helium ion microscopy (HIM) images of crystalline metal clusters requires microscopic understanding of the effects of He ion irradiation on the system, including energy deposition and associated heating, as well as channeling patterns. While channeling in bulk metals has been studied at length, there is no quantitative data for small clusters. We carry out molecular dynamics simulations to investigate the behavior of gold nano-particles with diameters of 5-15 nmunder 30 keV He ion irradiation. We show that impacts of the ions can give rise to substantial heating of the clusters through deposition of energy into electronic degrees of freedom, but it does not affect channeling, as clusters cool down between consecutive impact of the ions under typical imaging conditions.

At the same time, high temperatures and small cluster sizes should give rise to fast annealing of defects so that the system remains crystalline. Our results show that ion-channeling occurs not only in the principal low-index, but also in the intermediate directions. The strengths of different channels are specified, and their correlations with sputtering-yield and damage production is discussed, along with size-dependence of these properties. The effects of planar defects, such as stacking faults on channeling were also investigated.

Finally, we discuss the implications of our results for the analysis of HIM images of metal clusters.

5:20pm **HI+AS+CA-WeA-10 Low Damage Imaging of Polymers with the Helium Ion Microscope**, ***Doug Wei**,* Carl Zeiss, RMS, Inc.*; J Notte,* Carl Zeiss PCS, Inc.*; A Stratulat,* Carl Zeiss Microscopy, Ltd., UK

Polymers present a combination of challenges for high magnification imaging with the conventional SEM or FIB. Because they are electrically insulating, polymers are susceptible to charge accumulation and can produce imaging artifacts. Or worse, the implanted charge and surface charge can generate fields large enough to induce catastrophic dielectric breakdown. The interaction of the primary beam with the chemical bonds can cause radiolysis, cross-linking, and chain scissions which alter their morphology and other properties. Ion beams of relatively heavy species (Ga and Xe) can cause appreciable sputtering especially at high magnifications. In some cases, the sputtering can be preferential for light atoms, causing disproportionate hydrogen loss. Further difficulties include heating effects, since the typical polymers are good thermal insulators. Compounding matters, they are often temperature sensitive and can be damaged at even modest temperature rises ~ 50 deg C.

However, some of the newly available light ion beams (H, He, Li) offer unique advantages that help to circumvent the problems traditionally encountered when imaging polymers. First, the charging effects are greatly diminished compared to the SEM. In part, this is because the incident ion is likely neutralized as it enters the sample, and remains in a mostly neutral state as it penetrates deeply. This leaves only a net surface charge, which is overall positive and made more so by the ejection of secondary electrons from the surface. This is easily resolved using a collection of low energy electrons provided by a flood gun. The light ion beams also have relatively low sputtering rates compared to the heavier ions. Their interactions are primarily with the electrons of the sample. So while they can affect bonding, they are much less likely to cause sputtering. The light ions will generally be implanted deeply, often hundreds of nanometers under the surface, and helium in particular is known to diffuse out over time. Thermal effects are also much reduced with the light ion beams compared to heavier ions or the SEM. The ion's initial kinetic energy is converted to random thermal energy over a relatively large volume. And much of the transferred energy goes to the electrons in the sample, and their relatively long mean free path helps to dissipate this energy into a larger volume.

Numerous imaging examples will be provided from a variety of polymers using the helium beam from the Zeiss ORION NanoFab. These serve as representative examples of the unique sample interaction of light ions and the advantages they offer for imaging polymers.

5:40pm **HI+AS+CA-WeA-11 Imaging of Biological Cells with Helium-Ion Microscopy**, ***Natalie Frese**, A Beyer, C Kaltschmidt, B Kaltschmidt,* Bielefeld University, Germany*; A Thomas,* Institute for Metallic Materials Dresden, Germany*; W Parak,* University of Hamburg, Germany*; A Gölzhäuser,* Bielefeld University, Germany

Studies from the last decade have shown that helium-ion microscopy (HIM) is suitable for studying biological samples. In particular, cell membranes can be imaged by HIM without metallic coatings, which could lead to disturbance of the surface. In this contribution, we give two examples of biological cells imaged by HIM: (i) mouse hippocampal neurons on patterned surfaces for neuronal networks and (ii) human cells treated with colloidal nanoparticles [1, 2]. Both examples benefit from the high resolution imaging of uncoated, biological materials by HIM, as for (i) the cell adherence to patterned surfaces could be imaged and for (ii) cell morphology images indicated harmful effects of colloidal nanoparticles to cells.

[1] M. Schürmann et al., PLoS ONE 13(2), e0192647 (2018)

[2] X. Ma et al., ACS Nano 11(8), 7807-7820 (2017)

6:00pm **HI+AS+CA-WeA-12 Channeling in the Helium Ion Microscope**, ***Hussein Hijazi**, L Feldman, R Thorpe, M Li, T Gustafsson,* Rutgers University*; D Barbacci, A Schultz,* Ionwerks

The helium ion microscope (HIM) has become a unique tool for modern materials science due to its high lateral resolution for imaging, high spatial resolution and nano-scale analysis. For crystalline materials, the incident beam may undergo ion channeling, which strongly modifies all of the basic ion-solid interactions associated with these HIM functions. Here, a 30 keV He^+ beam was used for RBS channeling in a W(111) crystal using a novel time of flight (HIM/TOF) detector developed at Rutgers University to extract critical channeling parameters. Measurements of the minimum backscattering yield (χ_{min}), surface peak (SP), and critical angle, are compared to several theoretical estimates. The results illustrate the advantage of using channeling in a backscattering mode to characterize crystalline materials with the HIM, as the backscattering intensity modifications are far greater for scattered ions than for secondary electrons. This case of "ideal" channeling with the HIM now provides a basis for analysis of more complex materials such as polycrystalline materials and textured structures, and quantifies the role of HIM induced materials modification in crystalline materials.

Nanometer-scale Science and Technology Division
Room A222 - Session NS+2D+AS-WeA

Probing and Modifying Surface and Interfacial Chemistry at the Nanoscale

Moderators: Phillip First, Georgia Institute of Technology, Adina Luican-Mayer, University of Ottawa, Canada

2:20pm **NS+2D+AS-WeA-1 Bitumen's Microstructures are Correlated with its Bulk Thermal and Rheological Properties**, *X Yu,* Worcester Polytechnic Institute*; S Granados-Focil,* Clark University*; M Tao,* ***Nancy Burnham**,* Worcester Polytechnic Institute

Understanding of how the chemistry of asphalt binders (i.e., bitumens) affects their bulk properties is critical for development of structure-related mechanical models and performance-based specifications for asphalt binders, including mitigation of potholes and improved recycling of this non-renewable material. However, establishing the chemical-mechanical relationships that govern asphalt binders' properties remains a challenge due to binders' complex chemical makeup [1] and the intriguing dynamic molecular interactions among binders' various chemical constituents. [2] Here, we investigate the effect of chemical composition on binders' microstructure and thermal and rheological behavior. Two virgin binders from different crude oil origins were chosen and a series of derivative binders was made by remixing different weight ratios of the asphaltenes and the maltenes obtained from the two source binders. Thermal and rheological properties of all binders were measured using modulated differential scanning calorimetry and dynamic shear rheometry, respectively. Binders' microscopic characteristics (e.g., nano- and micro-structures and their contrast in phase images) were evaluated using atomic force microscopy. In bitumens with more miscibility between the asphaltenes and maltenes, the samples appear to undergo a sol-gel transition as the asphaltene concentration increases above 25%. In less miscible bitumens, micro-scale phase segregation is readily apparent at the surface. Our results show that bitumens' characteristic microstructures, as a result of the complex molecular interactions among their various chemical components, are correlated with their bulk thermal and mechanical properties. Notably, the asphaltene/maltene ratio alone cannot predict a bitumen's bulk properties. Instead, a bitumen's distinctive microstructures and its colloidal miscibility index provide meaningful insights into the effect of chemical composition on glass transition, phase stability, and rheological properties of the bitumen, which may in turn help improve the sustainability and design of roads. [3]

1. X. Yu et al., Adv. Colloid Interface Sci. 218, 17-33 (2015).

2. X. Yu et al., Energy & Fuels 32, 67-80 (2018).

3. X. Yu et al., submitted

2:40pm **NS+2D+AS-WeA-2 Energetics and Statistical Mechanical Analysis of Complexation on Metal Surfaces**, *J Lee, J Evans, T Windus, P Thiel,* ***Da-Jiang Liu**,* Ames Laboratory and Iowa State University

Stabilities of metal-ligand complexes on surfaces are crucial for the process of self assembly of 2D structures. We provide a comprehensive theoretical assessment at the level of Density Functional Theory (DFT) of the stability of various coinage metal-sulfur complexes, M_mS_n, with M=Cu, Ag, and Au, both in the gas-phase and also for these complexes adsorbed on the (111) and (100) surfaces of the same coinage metal. An early influential theoretical study on S/Cu(111) proposed that the Cu-$_3$S$_3$ complex being the most stable copper containing species. Later combined low temperature STM and DFT studies suggest that a heart-shaped Cu$_2$S$_3$ and its concatenations being more stable. Larger and even more complex Ag-S complexes have being observed for S/Ag(111). No complexation have been observed for S/Cu(100) and S/Ag(100). On the other hand, a Au$_4$S$_5$ complex and its fragmentations have being observed for S/Au(100), but no complexation is observed for S/Au(111) at low S coverage. We select a set of nine types of complexes, chosen for their proposed existences, intrinsic stabilities, and affinities for adsorption on metal surfaces. For the adsorbed species, we calculate various aspects of their energetics including their formation energy from sulfur adsorbed on terraces and from metal atoms that are in thermal equilibrium with the substrate. From this perspective, our DFT analysis shows that Ag$_2$S$_3$, Ag$_3$S$_3$ and many larger complexes on Ag(111) are strongly stable, Cu-$_2$S$_3$ is stable and some larger complexes are marginally stable on Cu(111), but only Au-$_4$S$_4$ on Au(111) is stable. In contrast, no complex is stable on Cu(100) and Ag(100), but a group of complex is stable on Au(100), with Au$_4$S$_5$. DFT results are consistent with experiments with the apparent exception of Au(111). This comprehensive assessment of energetics provides key input for statistical mechanical analysis of S adlayer ordering in the absence of complexation, and of the kinetics of complex formation and associated enhanced mass transport and surface dynamics.

3:00pm **NS+2D+AS-WeA-3 Adding the Chemical Dimension to Lithography at All Scales: Enabling Cellular Therapies & Other Adventures in Biology and Medicine***, **Paul S. Weiss**[1],* University of California, Los Angeles **INVITED**

By controlling the exposed chemical functionality of materials from the submolecular through the centimeter scales, we have enabled new capabilities in biology, medicine, and other areas. I will discuss current and upcoming advances and will pose the challenges that lie ahead in creating, developing, and applying new tools using these capabilities. These advances include using biomolecular recognition in sensor arrays to probe dynamic chemistry in the brain and microbiome systems. In other areas, we introduce biomolecular payloads into cells for gene editing at high throughput for off-the-shelf solutions targeting hemoglobinopathies, immune diseases, and cancers. These methods use specific chemical functionalization and control of surface contact and adhesion in microfluidic channels.

4:20pm **NS+2D+AS-WeA-7 STM Directed Synthesis of Armchair Graphene Nanoribbons and Their Oxidation***, C Ma,* Oak Ridge National Laboratory*; Z Xiao,* North Carolina State University*; A Puretzky, **Arthur Baddorf**,* Oak Ridge National Laboratory*; W Lu,* North Carolina State University*; K Hong,* Oak Ridge National Laboratory*; J Bernholc,* North Carolina State University*; A Li,* Oak Ridge National Laboratory

Highly controlled synthesis of graphene nanoribbons (GNRs) can be performed on a surface by polymerization of a selected precursor. Typically, this polymerization involves surface-assisted cyclodehydrogenations during thermal activation on catalytic metal surfaces. We have shown that armchair edge GNRs can be synthesized with 7, 14, and 21 carbon atom widths by absorbing 10,10'-dibromo-9,9'-bianthryl (DBBA) precursor molecules on Au(111).[1] Synthesis follows a two-step process of which the first step is polymerization at 470 K. The second step, cyclodehydrogenation, can be promoted globally by annealing to 670 K, or locally following hole injection using a scanning tunneling microscope (STM) tip.[2] Wider 14 or 21-aGNRs were formed when two or three 7-wide GNRs were conjugated side-by-side via inter-ribbon cyclodehydrogenation at the edge sites. Scanning Tunneling Spectroscopy (STS) reveals an electronic band gap dependent on the ribbon width. Bandgaps of ~2.6, ~0.3, and ~0.7 eV are measured for 7, 14, and 21 GNRs respectively, consistent with expectations of simple models.

For practical applications, understanding the stability of GNRs to oxidation is important. We have examined the thermal stability of 7-aGNRs after exposure to air.[2] Combining STM, Raman spectroscopy, x-ray photoemission spectroscopy, and first-principles theory calculations, the armchair GNRs are found to oxidize first at the zigzag ends while the edges remain stable. Oxygen attaches to the zigzag ends at temperatures as low as 180°C. Armchair edges are stable up to 430°C and become oxidized only above 520°C. Two oxygen species are identified, one a hydroxyl (OH) and the second atomic oxygen bridging two carbons, both of which are common in oxidized graphitic lattices. The bandgap is significantly reduced from 2.6 eV to 2.3 eV in the vicinity of the hydroxyl and to 1.9 eV near bridging O. These results suggest that the oxidization will significantly affect the transport properties of GNRs and provide parameters useful for maintaining integrity of GNRs during processing for devices.

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

1. C. Ma, et al., *Nano Letters* 17, 6241 (2017).

2. C. Ma, et al., *Nature Communications* 8, 14815 (2017).

3. C. Ma, et al., *Physical Review Materials* 2, 014006 (2018).

4:40pm **NS+2D+AS-WeA-8 Carbon-based Two-dimensional Materials from Surface-catalyzed Reactions of Small Molecules***, M Wolf, C Gerber, **Rebecca Quardokus**,* University of Connecticut

Aryl halides undergo an Ullmann-like coupling reaction on surfaces to yield a carbon-based two-dimensional material. 1,2-dibromobenzene couples to Au(111) lifting the gold herringbone reconstruction. The reaction intermediates and coupled gold atoms are mobile on the surface at 4 K. The FCC and HCP sections of the underlying gold substrate shift to new positions. Annealing the dibromobenzene on Au(111) decouples the intermediates from the gold. The gold herringbone reconstruction returns and a covalently-bonded carbon-based network forms on the Au(111) surface.

5:00pm **NS+2D+AS-WeA-9 Bottom-up Fabrication of 2D Molecular Networks via On-surface Reactions***, **Sabine Maier**,* University of Erlangen-Nürnberg, Germany **INVITED**

On-surface synthesis has attracted significant attention in recent years due to its potential to fabricate novel low-dimensional nanomaterials with atomic precision. In order to understand and control the synthesis of high-quality low-dimensional nanostructures, many efforts have been made to steer the reaction pathway by the design of smart precursors and by applying templating effects from the substrate. One of the challenges is the fabrication of long-range ordered two-dimensional covalently-linked networks via on-surface reactions. In contrast to molecular self-assemblies that are constructed by non-covalent bonds, the irreversible nature of the covalent bonds limits the structural control, which results in small domains and defects.

In my presentation, I will focus on recent high-resolution scanning probe microscopy experiments in combination with density-functional theory about the bottom-up fabrication and electronic properties of atomically precise one- and two-dimensional molecular nanostructures on metals.[1-4] Thereby, the effect of the flexibility, the symmetry, and chirality of the precursor molecules on the structure formation of covalently-linked molecular structures will be discussed. In particular, I will outline how well-ordered nanoporous 1D and 2D covalent molecular structures can be fabricated by use of debromination coupling reactions. We demonstrate the narrowing of the electronic band gap by increasing the π-system in covalently-linked structures and also show delocalized electronic states in surface-supported organometallic networks. Finally, I will conclude with a comparison of the structure formation of molecular nanostructures on bulk insulators and metal surfaces.

[1] C. Steiner et al. *Nature Communications***, 2017**, 8, 14765.

[2] M. Ammon, T. Sander, S. Maier, *J. Am. Chem. Soc.*, **2017** 139 (37), 12976–12984.

[3] Z. Yang et al. *Nanoscale*, **2018**, 10, 3769-3776.

[4] X. Zhang et al., ACS Nano, **2019**, 13 (2), 1385–1393.

5:40pm **NS+2D+AS-WeA-11 Determining the Jahn-Teller Stabilization Energy of Surface Vacancies on Si(111)-√3 x √3:B***, **Daejin Eom**,* Korea Research Institute of Standards and Science, Republic of Korea*; C Moon,* Korea Research Institute of Standards and Science*; J Koo,* Korea Research Institute of Standards and Science, Republic of Korea

The vacancy defect on the Si surface becomes increasingly important with the device scaling because it works as the charge trapping and scattering center with varying ionization states. Yet its characteristics have not been addressed as comprehensively as the bulk vacancy in Si. In fact, its behavior would be affected by the gap state evolution and the Fermi level pinning on the Si surface. On the other hand, the (111)-surfaces of Si come to have the √3 x √3 reconstruction instead of the 7 x 7 one when they are heavily B-doped [1,2]. This √3 x √3 surface does not evolve any energy state within the band gap, being contrary to the 7 x 7 one [2]. Also, the Fermi level is

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[1] **NSTD Recognition Award**

shifted to the valence band maximum on the √3 x √3 surface whereas it is pinned in the middle of the gap on the 7 x 7 surface [2]. Hence the vacancy defects on the two surfaces may have dissimilar characteristics from each other. Here, we generate the vacancy defects on the √3 x √3 surface via the atom manipulation technique and measure their structural and electronic properties by using the scanning tunneling microscopy and spectroscopy. We find that, unlike the 7 x 7 surface, the vacancy defects on the √3 x √3 surface are Jahn-Teller distorted in the ground state, but undergo the symmetry-restoring transition when gated by the external bias. We also determine the energy gain or stabilization energy of the Jahn-Teller transition quantitatively. These findings would extend our knowledge on the surface vacancies on Si and eventually contribute to the fabrication of better-performing nanometer-scale devices.

[1] I.-W. Lyo, E. Kaxiras, and Ph. Avouris, Phys. Rev. Lett. **63**, 1261 (1989).

[2] D. Eom, C.-Y. Moon, and J.-Y. Koo, Nano Lett. **15**, 398 (2015).

6:00pm **NS+2D+AS-WeA-12 Influence of the Substrate on Self-Assembly: Terphenyl Monolayers investigated by NC-AFM and FM-KPFM***, **Niklas Biere**[1], Experimental Biophysics & Applied Nanoscience, University of Bielefeld, Germany; S Koch, P Stohmann, Y Yang, A Gölzhäuser,* Physics of Supramolecular Systems and Surfaces, University of Bielefeld, Germany*; D Anselmetti,* Experimental Biophysics & Applied Nanoscience, University of Bielefeld, Germany

Carbon Nano Membranes (CNM) are mechanical stable and homogeneous quasi-2D systems, which are formed by electron radiation induced, cross-linked self-assembled monolayers (SAM). Contrary to graphene, the CNM structural and functional properties can be tailored by the selection of precursors for the SAM formation [1]. CNMs show the capability to act as a molecular sieve to filter e.g. water molecules from impurities with extraordinary efficiency [2]. While this result promises remarkable applications, the actual process of CNM formation as well as their structure and the mechanism for water permeation is still in the focus of our investigations. Furthermore, the choice of substrate influences the self-assembly of our precursor molecules more than previously expected, even with isoelectronic surfaces like gold and silver. In this work, we will present data acquired by noncontact-AFM combined with FM-KPFM under ultra-high vacuum conditions to investigate and compare the morphology of in-situ prepared SAMs and CNMs of terphenylthiols on Au(111) and Ag(111).

[1] A. Turchanin, A. Gölzhäuser, Adv. Mater. 28 (2016) 6075-6103.

[2] Y. Yang et al., ACS Nano 12 (2018) 4695-4701.

New Challenges to Reproducible Data and Analysis Focus Topic
Room A124-125 - Session RA+AS+BI-WeA
Addressing Reproducibility Challenges using Multi-Technique Approaches

Moderators: Tony Ohlhausen, Sandia National Laboratory, Vincent Smentkowski, GE Global Research Center

2:20pm **RA+AS+BI-WeA-1 Responding to New and Old Challenges to Data, Analysis and Scientific Study Reproducibility***, **Donald Baer**,* Pacific Northwest National Laboratory*; I Gilmore,* National Physical Laboratory, UK

An increasing number of studies, surveys and editorials highlight experimental and computational reproducibility and replication issues that frequently appear in most areas of modern science. In a 2018 AVS conducted survey, 66% of those responding identified reproducibility as a significant issue. There are multiple and complex causes of what some have called a “reproducibility crisis,” which can impact materials, interface/(bio)interphase, vacuum and others sciences of importance to AVS members. Reproducibility challenges are not new, but now appear in both old and new forms requiring innovative solutions. Drivers influencing reproducibility problems include the increasingly multi-discipline, multi-method nature of much advanced science, increased complexity of the problems and systems being addressed, and the large amounts and multiple types of experimental and computational data being collected and analyzed in many studies. Such issues challenge experimental teams and the review process. Systematic and sustained efforts are needed to address the causes of reproducibility problems that can hinder the rate of scientific progress and lower public and political regard for science. The Focus topic New Challenges to Reproducible Data and Analysis aims to raise awareness of the challenges, examine the causes, impacts of reproducibility problems and explore approaches that can help address both the newer and older generation of reproducibility challenges. Some problems and solutions are easy to identify, even if not readily implemented. Other drivers and causes are less obvious and therefore harder to address. This talk will introduce the focus topic sessions, review key literature on the topic of reproducibility and summarize how the presentations fit together as a way to address reproducibility challenges.

2:40pm **RA+AS+BI-WeA-2 Achieving Reproducible Data: Examples from Surface Analysis in Semiconductor Technology***, **Thierry Conard**, P van der Heide, A Vanleenhove, C Zborowski, W Vandervorst,* IMEC, Belgium

Repeatability and reproducibility in surface analysis in the semiconductor industry are key to for supporting efficient process development as well as High Volume Manufacturing (HVM). As two examples, long term repeatability is critically important when comparing to historical data, while reproducibility is required to support technology transfers when HVM of specific devices is to be carried out at multiple sites. This however introduced a number of unique challenges for running a characterization facility.

In this presentation we will present a number of examples that can result in reproducibility issues. Particular focus will be in the areas of X-ray Photoelectron Spectroscopy (XPS) Secondary Ion Mass Spectrometry (SIMS). The first and foremost causes of repeatability and reproducibility arise from instrumental variation. A second important source arises from samples variability. We will show that assessing long-term instrumental stability is potentially hindered by long term variation of samples characteristics. We will also show that an understanding of the characterization techniques is paramount to understanding such issues.

Next to the “pure” technical causes of repeatability and reproducibility, is the human factor. This involve for instance decision making in data treatment during for example, fitting procedures, statistical treatments, etc. This will be illustrated using practical examples. And with present day characterization depending more heavily on computational support/ commercial software, potential detriments to characterization repeatability will again be made evident. Finally, we will show through round-robin results, that combining all the above factors, widely varying results can be obtained on the same samples.

3:00pm **RA+AS+BI-WeA-3 New Challenges in Analytical Reproducibility Illustrated with Old and New Case Studies***, **Thomas Beebe Jr**,* University of Delaware **INVITED**

To address the subject of this session's topic, "New Challenges to Reproducible Data and Analysis," I have chosen to select a few case studies from my research group's work over the past 30 years. My examples will therefore be drawn from the methods and techniques that I have employed: XPS, TOF-SIMS, AFM, STM, and from the surface-related fields in which we have worked: biomolecules on surfaces, molecular self-assembly, biomaterials, and perhaps some others. It has always been my goal and approach to employ careful controls, scientific statistics, and data extraction to the richest extent possible.

4:20pm **RA+AS+BI-WeA-7 Challenges and Approaches to Addressing Reproducibility in Biointerface Science and Engineering***, **Sally McArthur**,* Swinburne University of Technology and CSIRO. Australia, Australia **INVITED**

Our publications should serve as guides to repeat our experiments/analyses and reproduce the results; however, quite often we may find ourselves not able to do so. Over the past few years, there have been many papers and editorials that have shown that issues associated with Repeatability, Reproducibility, and Replicability impact almost all areas of science, and in an AVS-conducted survey, 65% of those responding indicated that they have seen or experienced significant reproducibility issues when they have sought to recreate experiments from the literature. It is clear that the increasing demands of complex research requiring use of multiple experimental and computational research methods is a central theme. The challenge in the Biointerface Science community is compounded by the inherent variability of biology. Working at the interface between the physical and life sciences, it is often difficult for us to have in-depth knowledge of the idiosyncrasies of the many techniques we use and we need to be aware of for our data interpretation. This talk will discuss approaches we are taking to tackle this issue within the Biointerface Science Community and the journal Biointerphases. We will look at how we can champion best practices, sharing our knowledge across our community, and seek to support researchers who are new to the field or want to explore new techniques to avoid the pitfalls and better

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[1] **NSTD Graduate Student Award Finalist**

understand both the opportunities and limitations of the techniques, methods, and approaches used in our multidisciplinary community.

Sally L McArthur, Editor Biointerphases

5:00pm **RA+AS+BI-WeA-9 Complementary Measurements of Colloidal Nanoparticles and their Coatings by In-situ and Vacuum-based Methods**, ***Caterina Minelli,*** National Physical Laboratory, UK **INVITED**

Engineered nanoparticles add high value to commercial products and have the potential to improve our quality of lives and boost prosperity. For example, they provide radical new approaches to cancer drug delivery, biosensing, medical imaging and catalysis. However, the effective implementation of these materials relies on the ability to measure and control their properties, such as their surface chemical identity, size and concentration. There are significant challenges in the analysis of nanomaterials due to, among other factors, the interdisciplinary nature of the field and the lack of adequate reference materials to calibrate analytical tools. The use of complementary tools provides opportunities for (1) deepening the quantitative understanding of these systems and, importantly, (2) a route to method validation. I will provide examples from our work on both these cases.

(1) We use a combination of methods to analyse nanoparticles which are employed in liquid media (*in-situ*) using techniques such as analytical centrifugation and dynamic light scattering and *ex-situ* with X-ray photoelectron spectroscopy (XPS). Sound sample preparation protocols are critical for meaningful and comparable measurements. This is especially important when using complementary methods for the analysis of the same samples. I will discuss our experience in the analysis of protein coated gold nanoparticles and polymeric core/shell nanoparticles and show how multimodal analysis is critical to the full understanding of the system.

(2) The lack of certified reference materials for nanoparticle number concentration has hindered the validation of laboratory methods, which resulted in a general distrust in commercially available instrumentation. We have led a collaborative effort to develop accurate methods based on small angle X-ray scattering (SAXS) and single particle inductively coupled plasma mass spectrometry (spICPMS) for the measurement of colloidal number concentration. We have then used these methods to assess and validate a range of laboratory methods. I will discuss the result of this work for both ideal and agglomerated nanoparticles and present the outcomes of a large VAMAS interlaboratory study which assessed four methods for the measurement of colloidal concentration.

Finally, I will look at unmet challenges in the characterisation of nanoparticles and discuss the benefits of a multimodal approach to them.

5:40pm **RA+AS+BI-WeA-11 Multiple Technique Analysis of Perovskite Materials used in Battery and Fuel Cell Components**, ***Robin Simpson****, P Mack, T Nunney,* Thermo Fisher Scientific, UK

Due to the worlds ever increasing energy needs, renewable sources, higher efficiency and energy storage have become important research areas. Therefore, full analysis of the materials used in such applications can add to our understanding of these emerging technologies. In many cases this will mean using several techniques on a single sample.

The chemical composition of the materials found in batteries or fuel cells play a huge part in the desired properties. An example of this is in the inclusion of Sr^{2+} in the A sites of lanthanum manganite. This increases the electronic conductivity of cathode material via the addition of electronic holes to the perovskite structure. XPS allows us to quantify the chemistry of the material and use that data to further improve its properties.

Chemical analysis of the surface of the material by XPS also allows us to identify diffusion or segregation effects that can occur once a battery material has been cycled. Once a build-up of surface material on an electrode becomes too thick ions cannot pass between them, preventing charging of a cell. Using XPS with other techniques like ISS allows us to characterise the surface material (~ top 10 nm) and the surface monolayer.

Here we discuss a LaSrFeCoO perovskite sample typically found in fuel cell and battery cell electrode materials. XPS is used to quantify the composition of the material and identify the La chemical bonding state to find the sample contains La_2O_3 bonding. ISS is also utilised to show no significant Fe and Co at the top surface of the sample. Comparing this to the XPS data taken from the top 10 nm of the shows signs of Fe and Co depletion at the surface.

The perovskite materials are also found in solar cell components. These materials are often used due to their high efficiencies but also because the material band gap is tuneable therefore allowing us to optimise the material composition. Using a technique like REELS combined with XPS can enable us to measure the band gap of the material to reveal the efficiency as well as identify the composition. In this case the band gap of the sample was calculated at 6.3 eV using REELS.

We will also be discussing the use of coincident XPS/Raman to investigate the bulk and surface characteristics of the LaSrFeCoO sample without exposing it to atmosphere between analysis.

6:00pm **RA+AS+BI-WeA-12 Mapping Local Physical Properties by Combining ToF-SIMS Analysis with Advanced Scanning Probe Microscopy**, ***Maiglid Andreina Moreno Villavicencio****, N Chevalier, J Barnes,* CEA-LETI, France*; P Kermagoret, F Lorut,* ST Microelectronics, France*; B Gautier,* Université de Lyon, France

The continuous miniaturization and complexity of micro-devices have pushed existing characterization techniques to their limits. The correlation of techniques has emerged to overcome this issue and provide precise and accurate characterization. We have focused our research on combining and studying the applications of two specific techniques: time-of-flight secondary ion mass spectrometry (ToF-SIMS) and atomic force microscopy (AFM). The ToF-SIMS is a high-performance technique to chemically analyze a sample in 3-dimensions with a lateral resolution of 100 nm. On the other hand, the AFM is a high-resolution technique to obtain maps of the topography and local physical properties with a lateral resolution of 10 nm.

A ToF-SIMS / AFM methodology that combine the topographical information with the chemical composition has been established [1]. It was used to achieve a topography-corrected 3D ToF-SIMS data set and maps of local sputter rate where the effect of roughness and vertical interfaces are seen. However, the correlation of these characterization techniques is not limited to these applications. Indeed, by using advanced operation modes of the AFM, maps of diverse physical properties of the sample can be obtained at the same time as the topography.

We have explored the combination of ToF-SIMS analysis with three AFM advanced modes: piezoresponse force microcopy (PFM), scanning capacitance microscopy (SCM) and scanning spreading resistance microscopy (SSRM). These operation modes respectively allow to map ferroelectric domains, to locally measure capacitance variations and to image the sample surface resistivity.

The combined ToF-SIMS / AFM methodology was applied ex-situ per individual AFM mode on diverse samples for applications focused on micro-electronics. We will present here some promising results highlighting the strength and the perspectives of the expansion of this combination to other applications.

[1] M.A. Moreno et al, J. Vac. Sci. Technol. B 36 (2018) 03F122.

Advanced Surface Engineering Division
Room A215 - Session SE+AS+TF-WeA

Nanostructured Thin Films and Coatings

Moderators: Mehran Golizadeh, Montanuniversität Leoben, Austria, Suneel Kodambaka, University of California Los Angeles

2:20pm **SE+AS+TF-WeA-1 Structural and Optical Properties of Pulsed-Laser Deposited β-Ga_2O_3 Thin Films**, ***Mallesham Bandi****, V Zade, R Chintalapalle,* University of Texas at El Paso

In the course of demand for wide band gap semiconductors in modern electronic devices, β-Ga_2O_3 is extensively studied for the last two decades due to its wide range of applications such as field effect devices, switching memories, high temperature gas sensors, photocatalysts, deep-UV photodetector and transparent conducting electrode etc. However, fabricating device quality thin films and understanding the optical properties is an active timely research to exploit β-Ga_2O_3 into wide range of optoelectronic device applications. We report on the effect of deposition parameters on the structure and optical properties of β-Ga_2O_3 fabricated by Pulsed Laser Ablation onto a wide range of substrate materials. Polycrystalline thin films were fabricated on silicon and sapphire substrates with varying substrate temperatures and oxygen partial pressures, which resulted in various morphologies. To study the effect of morphology on optical properties polycrystalline thin films were analyzed using spectroscopic ellipsometry. Moreover, epitaxial thin films of β-Ga_2O_3 were fabricated on C-plane sapphire and MgO (100) oriented substrates. A more detailed account of structure, growth behavior and optical properties of β-Ga_2O_3 will be presented and discussed.

2:40pm **SE+AS+TF-WeA-2 Structural, Electrical, and Optical Properties of Mo-Ga Alloy Thin Films***, **Nivedita Lalitha Raveendran,** R Chintalapalle,* University of Texas at El Paso

Materials with thermal stability and can establish a stable contact for component layers are highly desirable for the design and development of advanced high power electronic device technologies. In this context, the present study investigates the effect of growth temperature on the structural, morphological, optical and electrical properties of the thin films of rarely investigated Mo-Ga alloy system. The objective is to understand the growth behavior, structure, electronic properties and thermal stability of Mo-Ga thin films for application in Ga_2O_3 based devices. In the present work, Mo-Ga thin films of ~350 nm thickness were fabricated on Si (100) substrates by sputter-deposition. The deposition temperature was varied in the range of 25-700^{o}C. X-ray diffraction analysis of the deposited samples indicate the realization of nanocrystalline films at 500^{o}C, and beyond 500^{o}C deterioration in crystallinity was noticed. A shift in Bragg's position towards higher angle was evident with increase in substrate temperature, which could be attributed to substrate temperature induced residual stresses. Moreover, formation of non-stoichiometric thin films was observed at higher deposition temperature (>500^{o}C). The optical properties of the deposited thin films were obtained by spectroscopic ellipsometry and a detailed analysis of the electrical properties of the thin films were also carried out. The results will be presented and discussed to establish the structure-composition-property correlation.

3:00pm **SE+AS+TF-WeA-3 Metallic Glass: From Coating to First-Ever Nanotube Arrays***, **Jinn P. Chu,*** National Taiwan University of Science and Technology, Taiwan, Republic of China

Thin film metallic glass (TFMG) is a new class of multi-component metallic thin film with unique characteristics, including high strength, high ductility, smooth surface, absence of grain boundaries, low coefficient of friction, and corrosion resistance, though their bulk forms are already well-known for properties because of their amorphous structure. Thin films prepared by physical vapor-to-solid deposition are expected to be further from equilibrium than those prepared by liquid-to-solid melting or casting processes. This is expected to further improve the glass forming ability and widen the composition range for amorphization. In the first part of my talk, I will present some important TFMG properties and applications we have discovered in recent years. Then, the metallic glass nanotubes (MGNTs) on Si fabricated by a simple lithography and sputter deposition process for very large-scale integration is introduced. This first-ever metallic nanotube array is awarded by *American Chemical Society* (ACS) at nano tech Japan 2018 in Tokyo. Like biological nanostructured surfaces, MGNTs show some surprising water repelling and attracting properties. Nanotubes are 500-750 nm tall and 500-750 nm in diameter [1]. The MGNT surface becomes hydrophobic, repelling water. By heating/cooling the array, the surface hydrophobicity is changed. Two examples will be presented in this talk based on modifications of this scheme. First, after modification of biotin, the array acts as a waveguiding layer for an optical sensor. The MGNT sensor waveguide could readily detect the streptavidin by monitoring the shift. The detection limit of the arrays for streptavidin is estimated to be 25 nM, with a detection time of 10 min. Thus, the arrays may be used as a versatile platform for high-sensitive label-free optical biosensing [2]. Second, the array is prepared on a heating device and, with an applied electric voltage to the heating device underneath, so that the arrays are functioned as biomimetic artificial suckers for thermally adhesion response [3].

References

[1] J. K. Chen, W. T. Chen, C. C. Cheng, C. C. Yu and J. P. Chu, Metallic glass nanotube arrays: preparation and surface characterizations, Materials Today, 21 (2018), 178-185.

[2] W. T. Chen, S. S. Li, J. P. Chu, K. C. Feng, J. K. Chen, Fabrication of ordered metallic glass nanotube arrays for label-free biosensing with diffractive reflectance, Biosensors and Bioelectronics, 102 (2018), 129-135.

[3] W. T. Chen, K. Manivannan, C. C. Yu, J. P. Chu and J. K. Chen, Fabrication of an artificial nanosucker device with a large area nanotube array of metallic glass, Nanoscale, 10 (2018) 1366-1375.

3:20pm **SE+AS+TF-WeA-4 Tin Oxide Nanoaggregate Fragmentation and Restructuring during Supersonic Impaction based Thin Film Deposition Processes***, **Souvik Ghosh**, X Chen, C Li, B Olson, C Hogan,* University of Minnesota, Minneapolis

Aerosol deposition (AD) is a versatile technique for printing thin films. During AD, gas-suspended particles are impacted inertially on a target surface at high velocities. Subsonic impaction processes often lead to highly porous, weakly bound depositions. High-speed supersonic deposition, however, can lead to denser, mechanically robust coatings of metals & metal oxides. Supersonic deposition is hence a potential low temperature route to the additive manufacturing of thin films (<1 µm to >10 µm) of a variety of materials.

However, the mechanism of film densification & consolidation remains poorly understood, particularly because AD can function with spherical or fractal-like agglomerated particles, from both dry powder feeds & aerosol synthesis processes. In an effort to better understand AD, we examined the mechanism of thin film formation via supersonic impaction of SnO_2 nanoaggregates on alumina, where we observed the formation of mechanically robust SnO_2 thin films. SnO_2 nanoaggregates were synthesized via flame spray pyrolysis (FSP) of Tin 2-Ethylhexanoate. These nanoaggregates characterized via differential mobility analysis shows a broad size distribution in the 40 nm -300 nm mobility diameter range. X-ray diffraction analysis of as-collected powders confirmed the formation of nano-crystalline SnO_2. To understand morphological changes to aggregates during high speed deposition, a differential mobility analyzer was used prior to deposition to select aggregates within a prescribed mobility diameter. The aggregates were then deposited electrostatically at low velocity (at atmospheric pressure) & supersonic speeds after passing through a 200 µm throat width, slit-type, conically contoured converging-diverging nozzle. With low speed deposition, we observed highly branched, chain like aggregates; while after supersonic deposition, we observed denser aggregates with significantly lower number of particles. Images hence suggest that the aggregates fragment & restructure during supersonic impaction.

Fragmentation & restructuring was quantified by image analysis of TEM images to determine their projected radii of gyration, perimeter, end-to-end distance, & projected area. These four parameters were then compared to those from in-silico projections of quasifractal aggregates, enabling extrapolation of the 3D architectures of deposited particles. Plots of the number of primary nanoparticles in aggregates as functions of their inferred radii of gyration confirmed that supersonic deposition leads to both (1) fewer primary particles per aggregate (fragmentation) & (2) for a given number of primary particles, smaller radii of gyration (restructuring).

4:20pm **SE+AS+TF-WeA-7 From Gas-ion to Metal-ion-controlled Irradiation: A Paradigm Shift in the Thin Film Growth by Magnetron Sputtering***, **Grzegorz Greczynski,*** Linköping University, Sweden*; I Petrov, J Greene,* University of Illinois at Urbana-Champaign*; L Hultman,* Linköping University, Sweden **INVITED**

Ion irradiation is a key tool for controlling the nanostructure, phase content, and physical properties of refractory ceramic thin films grown at low temperatures (T_s) by magnetron sputtering. However, in contrast to gas-ion bombardment, the effects of metal-ion irradiation on properties of these films have not been extensively studied due to (i) low metal-ion concentrations during standard dc magnetron sputtering (DCMS), and (ii) difficulties in separating metal-ion from gas-ion fluxes. These issues were recently resolved with our development of high–power pulsed magnetron sputtering (HiPIMS), in which pulsed substrate bias is applied in synchronous to the metal-ion-rich portion of each pulse.[1] Careful choice of sputtering conditions allows exploitation of gas rarefaction effects such that the charge state, energy, and momentum of metal ions incident at the growing film surface can be tuned.

The results of time-resolved mass spectrometry analyses performed at the substrate position during HiPIMS and HiPIMS/DCMS co-sputtering of transition-metal (TM) targets in Ar and Ar/N atmospheres are reviewed. Knowledge of the temporal evolution of metal- and gas-ion fluxes is essential for precise control of the incident metal-ion energy and minimizing the role of gas-ion irradiation. Also, covered are the growth of TM nitride and boride alloys by metal-ion synchronized HiPIMS. In contrast to gas-ions, a fraction of which are trapped at interstitial sites, metal-ions are primarily incorporated at lattice sites resulting in much lower compressive stresses. In addition, the closer mass match with the film-forming species results in more efficient momentum transfer and provides the recoil density and energy necessary to eliminate film porosity at low T_s. Several novel film-growth pathways are described: (i) nanostructured N-doped *bcc*-$CrN_{0.05}$ films combining properties of both metals and ceramics, (ii) fully-dense, hard, and stress-free $Ti_{0.39}Al_{0.61}N$, (iii) single-phase cubic $Ti_{1-x}Si_xN$ with the highest reported SiN concentrations, (iv) unprecedented AlN supersaturation in single-phase NaCl-structure $V_{1-x}Al_xN$, (v) a dramatic increase in the hardness, due to selective heavy-metal-ion bombardment during growth, of dense $Ti_{0.92}Ta_{0.08}N$ and $Ti_{0.41}Al_{0.51}Ta_{0.08}N$ films deposited with no external heating, and (vi) simultaneous increase in both hardness and toughness of $Zr_{1-x}Ta_xB_y$ layers deposited with synchronized Ta^+ irradiation.

Finally, $Ti_{1-x}Ta_xN$ alloys grown with no external heating are shown to produce high-quality Cu diffusion barriers and provide excellent corrosion protection for stainless-steel substrates.

[1] G. Greczynski, J. Lu, J. Jensen, I. Petrov, J.E. Greene, S. Bolz, W. Kölker, Ch. Schiffers, O. Lemmer and L. Hultman, J. Vac. Sci. Technol. A 30 (2012) 061504

5:00pm **SE+AS+TF-WeA-9 Atomic Layer Deposition of Silver Thin Film on Polydimethylsiloxane (PDMS)***, **Sarah Hashemi Astaneh**, C Sukotjo, C Takoudis,* University of Illinois at Chicago

Two types of samples were prepared in this work:

1- Silver coated PDMS

2- Silver coated PDMS with interlayer of TiO_2

For type 1 samples: Silver deposition was done in the costume-built ALD system. (Ag(fod) (Pet_3)) was used as a silver precursor and dimethyl amineborane ((BH_3 ($NHMe_2$)) was used as a reducing agent. Silver bubbler and dimethyl amineborane bubbler temperatures were kept at 96 °C and 50 °C, respectively. The reactor pressure and temperature was kept at 500 mtorr and 115 ˚C during deposition, respectively.

For type 2 samples: prior to silver coating, deposition of TiO_2 on PDMS was done in a commercial ALD system (Kurt J. Lesker 150 LE). Tetrakis (dimethylamido) titanium (IV) (TDMAT™) was used as the metal oxide precursor and maintained at 70 °C in the bubbler during all depositions. Ultra high purity N_2 was used as a carrier gas as well as purging gas. O_3 was used as an oxidizer for this ALD reaction and it was prepared using a UV-ozone generator placed immediately upstream of the deposition chamber to reduce ozone decomposition in delivery line as described in our previous studies. The reactor pressure and temperature was kept at ~1000 mtorr and 120 ˚C during TiO_2 deposition. This process leads to ~9 nm of TiO_2 interlayer on PDMS.

Right after this step, TiO_2 coated PDMS samples were transferred to the custom-built ALD system and silver deposition was carried on in the costume-built ALD system similar to type 1 samples.

In each of the above runs, simultaneously; same thin film was deposited on p-type Si (100) silicon wafer (University wafer Inc, USA) and used as a reference substrate to determine deposited film thickness.

The growth and composition of the silver on top of PDMS samples were analyzed with X-ray photoelectron spectroscopy (XPS) using Kratos AXIS-165 equipped with monochromatic Al Kα X-ray source operating at 15kV and 10 mA. As can be seen in figure 1, Ag 3p, Ag 3d peaks appeared clearly on Si, TiO_2 coated Si and TiO_2 coated PDMS substrates.

5:20pm **SE+AS+TF-WeA-10 Fabrication of 2D Photonic Crystals using Block Copolymer Lithography on Flexible Substrates and Fibers for Wearable Technology***, **Wade Ingram**, R Spontak, J Jur,* North Carolina State University

Block copolymer lithography is a method of transferring a self-assembled pattern from the block copolymer to the substrate using vapor phase infiltration of metal or metal-organic precursors into select polymer domains. The process is able achieve sub-10 nm resolution and can be used for electronic or photonic device fabrication. In our research, we seek to use block copolymer lithography to template polymer films and textile fibers for applications in wearable electronics and advanced light absorption in garments.

Deriving inspiration from nature, 2D photonic crystals are fabricated using polystyrene-block-polymethylmethacrylate (PS-b-PMMA) copolymers. Through thermal and solvent vapor annealing, the block copolymer self-assembles into uniform domains with long-range order across the substrate. Subsequent exposure to common gas precursors like trimethylaluminum will result in a hybrid material forming from the exposed carbonyl functional groups in the PMMA domain. Etching steps in O_2 plasma or selective solvents results in a patterned nanostructure of the metal or metal-organic material deposited on the substrate. These structures are imaged using scanning electron microscopy before and after etching, as well as with atomic force microscopy in tapping mode to understand how robust they are. Further characterization using infrared and ultraviolet-visible spectroscopy is performed to generate plots showing how these unique nanostructures interact with light from UV through IR wavelengths. This work aims to understand how block copolymer lithography on polymeric and flexible substrates can eventually be applied to polymer fibers for functional textiles.

5:40pm **SE+AS+TF-WeA-11 Use of an Einzel Lens to Enhance Electrohydrodynamic Printing Technology***, **Matthew Strohmayer**[1], A Dhall, P Ramesh, N Tokranova, C Ventrice, Jr.,* SUNY Polytechnic Institute

Additive manufacturing (AM) shows great promise for both research and industrial applications. The main advantages of AM include limited waste and the ability to build complicated structures. The most common techniques for AM are fused deposition manufacturing, digital light printing, and ink jetting. All of these techniques suffer from resolution and material limitations. Recently, a cost-effective, versatile method of high-resolution printing called electrohydrodynamic (EHD) printing has been introduced. This method allows for spatial resolution in the hundreds of nanometers. This process works similarly to a typical ink jetting system, except instead of the ink/polymer being pushed out of a tip, it is pulled out by an applied electric field. This allows for the resultant droplet to be smaller than the needle diameter. Electrostatic repulsion of the charged droplets limits the ultimate resolution of this technique. To overcome this resolution limitation, we have incorporated an Einzel lens into the system to focus the droplets. This helps the droplets overcome the repulsive Coulomb interaction, leading to better spatial resolution. To validate this approach, simulations were performed to test for different parameters, including droplet size changes and lens optimization. This was then used to build a real system.

Surface Science Division
Room A220-221 - Session SS+AS+HC+OX-WeA

Reactions at Alloy Surfaces and Single Atom Catalysis

Moderators: Erin Iski, University of Tulsa, Bruce E. Koel, Princeton University

2:20pm **SS+AS+HC+OX-WeA-1 Correlating Structure and Function for Nanoparticle Catalysts***, **Graeme Henkelman**,* University of Texas at Austin **INVITED**

Metal nanoparticles of only 100-200 atoms are synthesized using a dendrimer encapsulation technique to facilitate a direct comparison with density functional theory (DFT) calculations in terms of both structure and catalytic function. Structural characterization is done using electron microscopy, x-ray scattering, and electrochemical methods. Combining these tools with DFT calculations is found to improve the quality of the structural models. DFT is also successfully used to predict trends between structure and composition of the nanoparticles and their catalytic function for reactions including the reduction of oxygen and selective hydrogenation. This investigation demonstrates some remarkable properties of the nanoparticles, including facile structural rearrangements and nanoscale tuning parameters which can be used to optimize catalytic rates. In this presentation I will focus on a pair of random alloy bimetallic nanoparticles which have complete different trends in hydrogenation activity as a function of composition. Pd/Au is found to be tunable as a function of composition whereas Pt/Au is not. The reason behind these different behaviors will be discussed.

3:00pm **SS+AS+HC+OX-WeA-3 Surface Reactivity of PtAg and PdAg: From Single-Atom Alloys to Supported Nanoparticles***, **Dipna Patel**[2,3],* Tufts University*; C O'Connor, R Madix, C Friend,* Harvard University*; E Sykes,* Tufts University

Catalytic hydrogenation reactions are important in many industrial applications. While Pt and Pd are catalytically active towards hydrogenation, they are often costly, and can suffer from poisoning by CO and coke. Previously, Ag based catalysts have been modified by alloying Pt or Pd for applications in highly selective heterogeneous catalysis. This has shown promise for catalyst design since Ag is cheaper and more resilient to poisoning. It is well known that ensemble size can dramatically change the catalytic pathway, however the atomic-scale structure of PtAg and PdAg alloys and their relation to catalytic activity is still unknown. Using scanning tunneling microscopy (STM) and STM-based spectroscopies, we characterized the surface structure and local geometry of Pt deposited on Ag(111) as a function of alloying temperature. At low temperatures, intermixing of PtAg is driven by a negative mixing enthalpy, resulting in

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[1] **ASSD Student Award Finalist**

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

[3] **National Student Award Finalist**

different metastable states such as isolated Pt atoms in, and islands on, Ag terraces, as well as Pt rich brims located along Ag step edges. Increasing the alloying temperature results in an increased concentration of Pt atoms along Ag steps edges as well as direct exchange of Pt atoms into Ag terraces. At higher temperatures, there is sufficient thermal energy for Pt atoms to fully disperse in the Ag(111) surface layer as isolated atoms, forming single-atom alloys. STM characterization of the surface structure of PdAg alloys reveals the formation of large Pd islands on Ag(111). Using STM, we investigated H_2 activation on active Pd sites and spillover on to Ag(111). The characterization of PtAg and PdAg surface alloys enables us to correlate reaction activity and selectivity to the atomic-scale structure of the alloy and to inform catalyst design that optimizes catalytic selectivity.

3:20pm **SS+AS+HC+OX-WeA-4 Single-site Catalysts by Metal-ligand Complexation at Surfaces: From Model Systems in Vacuum to High-pressure Catalysis on Oxide Supports*, Steven L. Tait,*** Indiana University

A grand challenge in heterogeneous catalysis is to achieve high levels of selectivity by controlling the chemical uniformity of metal catalyst sites at surfaces. Our group is working to apply principles of on-surface metal-organic redox assembly to develop a new approach to this problem. Metal-organic coordination networks at surfaces hold promise for selective chemical function, but there is a limited understanding of the chemical reactivity of these systems. Studies of model systems in ultra-high vacuum allow for detailed characterization of the structure and chemistry of these systems. We tested chemical activity of vanadium single-site complexes that are stabilized by tetrazine-based ligands and found activity toward dioxygen activation with a high degree of selectivity compared to vanadium nanoparticles. Reaction with O_2 causes an increase in V oxidation state from V^{II} to V^{IV}, resulting in a single strongly bonded V-oxo product and spillover of O to the Au surface [1]. The metal centers are stabilized in extended, ordered metal-organic complexes that self-assemble through an on-surface redox process on the Au(100) surface and are characterized by X-ray photoelectron spectroscopy, scanning tunneling microscopy, high-resolution electron energy loss spectroscopy, and density functional theory. New results extend these chemical studies to more complex systems that include bimetallic sites and redox isomer systems [2-3], which will also be highlighted in this presentation.

We have also developed synthesis schemes to assemble quasi-square planar metal-organic complexes on high surface area powdered oxides under ambient conditions through a modified wet-impregnation method. X-ray photoelectron spectroscopy measurements demonstrate loading of metal and ligand on the surface and synchrotron-based X-ray absorption spectroscopy measurements of the coordination shell of the metal centers demonstrates single site formation rather than nanoparticle assembly [4-5]. These systems are shown to be active for the catalysis of hydrosilylation reactions at a level that is competitive with current homogeneous catalysts. They also show excellent activity for hydrogenation in flow reactor experiment.

1. Tempas, Morris, Wisman, *et al.*, *Chem. Sci.*, **9**, 1674-1685 (2018). DOI: 10.1039/C7SC04752E

2. Tempas, Skomski, Cook, *et al.*, *Chem. Eur. J.*, **24**, 15852–15858 (2018). DOI: 10.1002/chem.201802943

3. Morris, Huerfano, Wang, *et al.*, *Chem. Eur. J.*, **25**, 5565-5573 (2019). DOI: 10.1002/chem.201900002

4. Chen, Sterbinsky, and Tait, *J. Catal.*, **365**, 303-312 (2018). DOI: 10.1016/j.jcat.2018.07.004

5. Chen, Ali, Sterbinsky, *et al.*, *ChemCatChem*, *in press* (2019).DOI: 10.1002/cctc.201900530

4:20pm **SS+AS+HC+OX-WeA-7 Controlling the Local Coordination and Reactivity of Oxide-supported Atomically Dispersed Pt-group Species*, Phillip Christopher,*** University of California at Santa Barbara **INVITED**

The synthesis of oxide supported Pt-group catalysts typically produces metal particles with dimensions of a few nanometers. Recent work has shown that Pt-group species can co-exist as nanoparticles and single atoms, and that careful synthetic approaches can produce exclusively single atoms. Interest in the reactivity of supported isolated Pt-group metal atoms stems from the maximized metal utilization efficiency, unique reactivity or selectivity, connection to organometallic catalysis, and the potential for making well-defined active sites. It has proven challenging to characterize the intrinsic catalytic activity of these dispersed active sites on oxide supports at a level that relates local electronic and geometric structure to function. The difficulty arises from their atomic dispersion, heterogeneity in the local coordination of active sites on most catalysts (i.e. isolated species sit at different sites on the support), dynamic changes in local coordination under reactive environments, and often the low loading of metal that is required to achieve site isolation.

In this talk I will describe a synthetic approach to produce isolated Pt-group atoms that exhibit uniformity in their bonding environment on an oxide support and show how a combination of microscopy, spectroscopy and theory can be used to describe the local coordination of these species. Then I will describe two different approaches to control the local environment of Pt-group atoms: (1) through varied pre-treatment that tunes the local coordination and oxidation state of the single atom, and (2) through the site selective deposition of single atoms near well-defined acid sites on oxide supports. Detailed characterization by a combination of spectroscopy and microscopy is used to develop structure-function relationships for these well-defined single atom active sites in the context of CO oxidation, methanol carbonylation and ethylene hydroformylation. This work highlights the ability to tune the local environment of single Pt-group atom active sites on oxide supports in analogous ways to the engineering of organometallic catalysts.

5:00pm **SS+AS+HC+OX-WeA-9 Coordination Defines Reactivity of a Model Single-atom Catalyst: Ir_1/Fe_3O_4(001)*, Zdenek Jakub*[1]**, *J Hulva, M Meier, U Diebold, G Parkinson,* TU Wien, Austria

The development of single-atom catalysts (SACs) was originally motivated by saving of the precious metal, but an equally intriguing characteristic of the ideal SAC is potentially high selectivity due to the high number of identical active sites. The coordination of the active metal center is known to play a crucial role in homogeneous catalysis, and in this talk, I will demonstrate that similar effects can be observed on a model single atom catalyst: Ir_1/Fe_3O_4(001). Using scanning tunneling microscopy (STM), noncontact atomic force microscopy (nc-AFM), temperature programmed desorption (TPD), x-ray photoemission spectroscopy (XPS) and DFT calculations, I will show that the coordination of single Ir_1 adatoms can vary depending on preparation, and that the local environment has dramatic consequences for the ability of the catalyst to adsorb CO. As deposited at room temperature, Ir atoms take 2-fold coordination to the surface oxygen atoms. Upon annealing, they incorporate into the first surface layer (5-fold coordinated Ir_1), and then into the first subsurface layer (6-fold coordinated Ir_1). The 2-fold adatoms can form both monocarbonyls and dicarbonyls, but the 5-fold Ir only binds a single CO. The structures are understood by analogy to square planar Ir(I) and octahedral Ir(III) complexes, respectively. The 6-fold Ir is coodinatively saturated, and thus deactivated for CO adsorption. These results show that control of the local coordination environment is critical to design so-called single-atom catalysts, and that incorporation into the support can be as critical a deactivation mechanism as thermal sintering.

5:20pm **SS+AS+HC+OX-WeA-10 Capturing the Early Stages of Oxidation on Low-Index Ni and Ni-Cr Surfaces*, William H. Blades,*** *P Reinke,* University of Virginia

The early stages of oxidation and corrosion of alloys control the structure and development of the oxide layer and therefore decisively influence its protective function. To this end, we have studied thenanoscale evolution of surface oxides prior to the formation of a complete layer. The oxidation of Ni(100), Ni(111), and Ni-Cr(100), Ni-Cr(111) surfaces was captured by sequential oxidization and measured with scanning tunneling microscopy/spectroscopy (STM/STS). The early-stage oxidation, and the influence of alloy composition and crystallographic orientation on surface reactivity, was studied by comparing pure Ni(100/111) and Ni-Cr(100/111) surfaces. Alloy thin films (8-18 wt.% Cr) were prepared on MgO(100/111) and exposed to oxygen up to 400 L at 773 K. Under these conditions, oxide nucleation is predicated by the development of oxygen adlayers on both the pure Ni(100/111) surfaces. The formation of a c(2x2)-O chemisorbed phase on the Ni(100) surface causes the step edges to facet into {100} segments, kinetically limiting NiO growth. However, no such faceting is observed on the Ni(111) surface and the nucleation and growth of NiO begins after only 300 L of O_2. Our experiments demonstrate that the addition of small amounts of Cr completely change the oxidation pathways. On the Ni-Cr(100) surface, the nucleation and growth of NiO initiates along the step edges, forming low-angle NiO wedges with a NiO-Ni(7x8) superstructure. Terrace oxide growth commences with the nucleation of small oxide particles, driven by the presence of Cr, which grow into large oxide nodules after further oxidation. NiO growth extends into the terraces and takes a NiO-Ni(6x7) cube-on-cube interfacial relationship. Several novel

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

surface reconstructions are observed and are tentatively attributed to Cr(100)-O reconstructions, suggesting surface segregation and phase separation of BCC Cr. Similarly, nano-sized oxide particles nucleate on the Ni-Cr(111) terrace and step edges, while single atomic NiO rows extend across the surface. Oxide nodules, similar to those found on the Ni-Cr(100) surface are observed and grow laterally along the terraces. Each of these aforementioned surface oxides present unique electronic signatures, and STS maps are used to quantify the spatial variations in their density of states and band gaps. The electronic heterogeneity of the surface underscores that the use a homogenous electric field to capture oxidation kinetics at the alloy-oxide interface should be revisited.

5:40pm **SS+AS+HC+OX-WeA-11 Evolution of Steady-state Material Properties during Catalysis: Oxidative Coupling of Methanol over Nanoporous $Ag_{0.03}Au_{0.97}$*,* *Matthijs van Spronsen,* Lawrence Berkeley National Laboratory*; B Zugic,* Harvard University*; M Salmeron,* Lawrence Berkeley National Laboratory*; C Friend,* Harvard University

Activating pretreatments can be used to tune both surface composition and surface structure of bimetallic alloy catalysts. Careful selection of both gas mixtures and reaction temperatures can lead to surfaces that are able to achieve optimum selectivity and activity under steady-state reaction conditions. The activation-induced changes in material properties of a nanoporous (np) $Ag_{0.03}Au_{0.97}$ alloy and their subsequent evolution under steady-state conditions for CH_3OH oxidation are presented. Initial activation by oxidation in O_3 at 423 K leads to the formation of AgO and Au_2O_3 driving a strong Ag enrichment in the near-surface region, based on ambient-pressure X-ray photoelectron spectroscopy (AP XPS) and extended X-ray absorption fine structure (EXAFS) analysis. Exposing this oxidized np $Ag_{0.03}Au_{0.97}$ to the O_2/CH_3OH reaction mixture reduces both Ag and Au oxides and results in a surface alloy locally highly enriched in Ag. Both the oxides and the highly Ag enriched alloy unselectively oxidize methanol to CO_2. However, at the reaction temperature of 423 K, the Ag slowly realloys with Au. Although decreasing, the composition remains enriched in Ag in the top few nanometers under steady-state conditions. The Ag content in the surface is 29 at.% in steady state and the desired product, methyl formate, is selectively produced without significant deactivation. The activation and evolution of the active phase is not uniform: nanometer-scale patches of AgO, leading locally to Ag-rich alloys, were observed with environmental transmission electron microscopy (E TEM). These local Ag-rich AgAu alloy regions are critical for initiation of the catalytic cycle through O_2 dissociation. Calculations based on density-functional theory (DFT) indicate that the O on the surface assist in stabilizing the Ag. Moreover, an essential factor for retaining this local enrichment in Ag is the modest reaction temperature of 423 K. At higher temperatures, bulk diffusion induces sintering and redistribution of the Ag, leading to a loss of activity. These findings demonstrate that material properties determining catalytic activity are *dynamic* and that metastable (kinetically trapped) forms of the material may be responsible for catalysis. Hence, catalytic activity and selectivity depend on the pretreatment, reaction temperature and gas composition. These observations provide guiding principles concerning the activation of heterogeneous catalysts for selective oxidation.

6:00pm **SS+AS+HC+OX-WeA-12 Reduction and Oxidation of Transition Metal Oxides: From Tailoring the Surface and Interface Properties to the New Crystalline Phases Formation***,* ***Dominik Wrana,*** Jagiellonian University, Poland*; C Rodenbücher,* Forschungszentrum Jülich GmbH, Germany*; K Cieślik, B Jany,* Jagiellonian University, Poland*; K Szot,* Forschungszentrum Jülich GmbH, Germany*; F Krok,* Jagiellonian University, Poland

In the recent years transition metal oxides have attracted tremendous interest, mostly due to the manifold real applications, ranging from (photo)catalysis, through memristive and neuromorphic device development, to energy storage and production. A specific quality which makes them so versatile is the ease by which their electronic and structural properties can be controlled by changing a cation's reduction state.

In this presentation we will present an overview of the impact that thermal reduction and oxidation have on the surface properties, which enable a precise control over the valence state of prototypical binary and ternary oxide representatives: TiO_2 and $SrTiO_3$. We will focus on the preparation methods under regular UHV conditions and upon additionally reduced oxygen partial pressure.

Reduction of both crystals results in the formation of oxygen vacancies and therefore d-electrons, which leads to changes in the work function and a corresponding rise in electrical conductivity, which could be tuned over many orders of magnitude [1]. A newly developed SPM-based technique, combining LC-AFM and KPFM, allows both measurements to probe the same area of the reduced $TiO_2(110)$ surface [2], helping understanding of the nanoscale resistive switching . Besides the change in electrical properties, the surface structure evolves towards nonstoichiometric reconstructions [1], due to the increased oxygen deficiency. Surprisingly, not only is oxygen flow possible during UHV annealing of the oxide crystal, but also incongruent cation sublimation can be triggered, as demonstrated for the perovskite oxides like $SrTiO_3$ [3]. Extremely low oxygen partial pressure (ELOP), achieved by the use of an oxygen-getter, initiates $SrTiO_3$ crystal decomposition and the formation of stable monocrystalline cubic TiO nanowires with a c(4x4) reconstructed surface [4]. Such bottom-up growth of conductive TiO nanostructures could be an alternative to other costly methods, resulting in the creation of the $TiO/SrTiO_3$ interface, with a sharp transition between Ti^{2+} and Ti^{4+} states, proven by atomically-resolved electron microscopy. This oxide heterostructure provides an interesting metal/insulator junction with a 0.6 eV work function difference [5], opening many new possibilities for (photo)catalysis and aiding in the search for exotic interface states.

[1] Wrana, D. et al. (2018) *Applied Surface Science*, *432*, 46-52.

[2] Rodenbücher, C. et al. (2018) *APL Materials*, *6*(6), 066105.

[3] Rodenbücher, C. et al. (2017) *physica status solidi (RRL)–Rapid Research Letters*, *11*(9), 1700222.

[4] Wrana, D. et al. (2019) *Nanoscale*, *11*(1), 89-97.

[5] Wrana, D. et al. (2019) Beilstein Arch., 201912.

Applied Surface Science Division
Room A211 - Session AS-ThM

Advances in Depth Profiling, Imaging and Time-resolved Analysis

Moderators: Jeffrey Fenton, Medtronic, Inc., Carl A. Ventrice, Jr., SUNY Polytechnic Institute

8:00am **AS-ThM-1 What Really Lies Beneath the AVS Surface? Depth Profiling Can Help Provide the Answer***, **Fred Stevie**, C Zhou, R Garcia,* North Carolina State University **INVITED**

Scratch the surface of the AVS and you will find a lot more than semiconductors. AVS Divisions range from electronic materials to thin films to vacuum technology to biomaterials.

Depth profiles obtained using AES, XPS, or SIMS have typically been used to provide in-depth elemental analysis. SIMS excels in depth resolution and detection limit. Rotation of the sample during analysis (Zalar rotation) can maintain good depth resolution for materials that do not sputter evenly. Application of electron beams aids the study of insulators. Standards can be created to quantify the elemental components. [1]

Analysis in depth of biomaterials has shown tremendous strides as the sources used to remove material have evolved. Initial studies of depth profiles with argon, then molecular beams such as SF_5^+, larger still with C_{60}^+, and now cluster beams with argon produced ever higher secondary ion yields and made possible in-depth analysis without loss of chemical state. Continued development has resulted in three-dimensional organic analysis. [2] Some success has been achieved for quantification of organic additives, especially when the additive contains an element not present in the matrix. [3-4]

A significant limitation is the achievable depth. Profiles are typically less than 100 µm. However, some technologies need depth information on a millimeter scale. Sample preparation methods, such as etching, beveling, cross sections, and back side analysis, can be employed. Cryogenic microtome can be used to obtain a cross section of organic layers subsequently analyzed with ToF-SIMS. [5] EDS can provide in depth information on samples where material has been removed at a series of depths using FIB. [6] The emergence of plasma FIB (PFIB) instruments with microamp currents makes possible deeper profiles and exposure of larger areas for analysis by other techniques. The xenon plasma FIB can remove material as much as 50 times faster than a conventional gallium FIB. [7,8]

[1] Secondary Ion Mass Spectrometry, F. A. Stevie, Momentum Press (2016)

[2] J. Bailey, R. Havelund, A. G. Shard, I. S. Gilmore, M. R. Alexander, J. S. Sharp, D. J. Scurr, ACS Appl. Mater. Interfaces 7, 2654 (2015)

[3] Chaunzhen Zhou, Fred A. Stevie, Stephen C. Smith, J. Vac. Sci. Technol. B36, 03F115 (2018)

[4] S. C. Smith, C. Zhou, F. A. Stevie, R. Garcia PLOS ONE 13, e0209119 (2018)

[5] C. Zhou, D. Sun, R. Garcia, F. Stevie, Anal. Methods 10, 2444 (2018)

[6] R. Garcia, F. A. Stevie, L. Giannuzzi, Microscopy and Microanalysis Proceedings (2019)

[7] Noel S. Smith, John A. Notte, and Adam V. Steele, MRS Bulletin 39, 330 (2014)

[8] www.tescan.com/en-us/technology/fib-sem/

8:40am **AS-ThM-3 TOF-SIMS Tandem MS Imaging of (Sub-)Monolayer Coatings for Device Processing***, **David M. Carr**, G Fisher,* Physical Electronics

One common objective in research, failure analysis and reverse engineering is to ascertain the 2D/3D composition and structure of molecules in devices as a result of various processing steps. Often there is insufficient background information and a lack of reference spectra to properly interpret the analytical observations. Two device processing case studies will be presented highlighting the benefits of adding MS/MS imaging to conventional TOF-SIMS experiments. The data was acquired on a PHI *nanoTOF* II designed for simultaneous TOF-SIMS (MS^1) imaging and tandem MS (MS^2) imaging [1-4].

In the first case study, a carbon residue was observed by Auger electron spectroscopy (AES) imaging on e^- beam lithography-patterned and etched device structures. TOF-SIMS tandem MS imaging was applied to characterize the composition and structure of the sub-monolayer residues. In the second case study, functionalized molecules containing bipyridine and triphenylphosphine ligands were patterned by a photolithography method and loaded with metals including Au, Pd and Pt [5]. TOF-SIMS tandem MS imaging was employed to confirm the presence and elucidate the structure of metal-organic ligands.

References

[1] G.L. Fisher, *et al*, *Anal. Chem*. **88** (2016) 6433-6440.

[2] G.L. Fisher, *et al*, *Microscop. Microanal*. **23** (2017) 843-848.

[3] C.E. Chini, *et al*, *Biointerphases***13** (2018) 03B409.

[4] T. Fu, *et al*, *Nature Sci. Rep*. (2018) accepted 06 December 2018.

[5] R. Müller and A. Welle at Karlsruhe Institute of Technology (KIT) and C. Barner-Kowollik at Queensland University of Technology (QUB) are acknowledged for providing the samples for analysis.

9:00am **AS-ThM-4 TOF-SIMS at the Edge***, **Alan Spool**, D Bilich,* Western Digital Corporation

TOF-SIMS instruments are designed to extract secondary ions in the direction normal to the surface by creating a potential difference between the sample and the extraction device. The optimum geometry for getting the highest transmission is for the sample to consist of a functionally infinite flat plane. When sample topography deviates from this ideal significantly, secondary ion transmission is reduced. The effect on the yield of each secondary ion is a function of the ion mass, but also the initial ion emission angular and momentum magnitude distributions. The yields of the lightest atomic ions are least affected by topography, and the yields of heavier molecular fragments and ions most significantly affected.

To quantitatively explore these effects, two samples presenting topographic challenges were used in this study.

1. The edge of a magnetic recording disk is tightly controlled and therefore reproducible. The disk is extremely flat. The surface produces homogeneous signals for atomic species and molecular fragments of the disk lubricant and adsorbed hydrocarbons and other organic species where ion yield is not affected by topography. There is a slight bevel at the edge, much smaller in size than the edge effect on secondary ion collection. The sample height drop off past the edge in this experiment was effectively infinite.

2. A Si coupon was etched to produce a deep enough crater that ion yields from the crater bottom were affected by the topography. A lighter etch was performed over a wider area sufficient to reach dynamic equilibrium (and thus produce a surface damaged identically to that at the crater bottom). The sample was then exposed to air and allowed to oxidize and be contaminated by adventitious organics before analysis. This sample represents the condition where at a distance from the sample, the surface is essentially flat, but near to the surface the ion extraction will see non-normal fields that affect secondary ion trajectories.

With these samples, it was possible to look at the effect of the topography on the yields of a variety of secondary ions, and at a variety of instrumental conditions, both in the IonTof TOF-SIMS 5 and in the Physical Electronics NanoTof II. The analysis results of the two types of topographic challenges are shown to be differently affected by instrumental conditions. No one condition gives the ideal remediation for all topographic challenges.

The work with the edged sample promises to provide a simple test for differences in the initial angular and momentum magnitude distributions. Such distributions may provide added clues to secondary ion formation mechanisms.

9:20am **AS-ThM-5 Variation of SIMS Secondary Ion Yield of Si and Mg Dopants in GaN Grown by MOCVD***, **M. K. Indika Senevirathna**,* Clark Atlanta University*; A Kozhanov, M Vernon, G Cross,* Georgia State University*; G Cooke,* Hiden Analytical Ltd, UK*; M Williams,* Clark Atlanta University

We present a study of the secondary ion yield of silicon and magnesium dopant species as a function of the primary ion beam energy in n-doped and p-doped gallium nitride, respectively. The epilayers were grown by metal organic chemical vapor deposition and depth profiled using a Hiden quadrupole secondary ion mass spectrometer. To our knowledge, this is the first such study for this matrix material system. The yields for oxygen and cesium primary beams were determined by varying the beam acceleration voltage of the primary ion beam from 0.5 kV to 5 kV at a fixed beam current. The results determine the primary beam energies for optimal species sensitivity.

9:40am **AS-ThM-6 Impact of the Molecular Weight on the Depth Profiling of Polymer Thin Films using Low Energy Cs$^+$ Sputtering***, **Amal Ben Hadj Mabrouk**,* Univ. Grenoble Alpes, CEA, LETI, Grenoble*; M Veillerot,* Univ. Grenoble Alpes, CEA, LETI, Grenoble, France*; A Chateauminois,* Soft Matter Science and Engineering Laboratory (SIMM), PSL Research University, France*; C Licitra,* Univ. Grenoble Alpes, CEA, LETI, Grenoble

Organic materials have been taking an increasing role in the world of electronic systems. They provide process compatibility, flexibility and adaptability in design, and the capacity for integration of electronic functions. They can be found in thin submicronic layers in various fields such as organic photovoltaic items or organic light emitting diodes . In order to determine and control the final device properties, it is of first importance to control the organic materials structural parameters during film growth or deposition. Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is able to provide such depth resolved relevant molecular information. Indeed, it has recently been shown that the ToF-SIMS sputtering response was sensitive to the molecular weight of thin polymer films bombarded with Argon gas cluster ions (Ar$_n^+$) [1].

In this work, we aimed to supplement these results when depth profiling is achieved with low energy cesium ions. We present the ToF-SIMS characterization of Poly (methyl methacrylate) and Polystyrene thin films [~100nm in thickness] with varying molecular weights (from 2 to 9.9x10^5 g.mol^{-1}) spin-coated onto silicon substrates. The characterization was carried out using monoatomic cesium source at different energies for sputtering and bismuth (Bi$_3^+$) ion source for analysis.

The evolution of the sputtering yield volume (nm^3/PI) of the polymer films has been measured with the molecular weight, thickness, temperature and for different energies of sputter beam. The results are considered with respect of previous results and interpreted considering polymeric material physical parameters such as the glass transition temperature (Tg).

[1] Cristaudo V., Poleunis C., Czerwinski B. and Delcorte A. (2014) *Surf. Interface Anal.*, 46, pages 79–82, doi: 10.1002/sia.5424 .

11:00am **AS-ThM-10 Probing the Surface Structure of Au-Pt Core-Shell Nanoparticles***, C Engelbrekt, **Ich Tran**, M Law,* University of California, Irvine

Au-Pt core-shell structures (Au@Pt) of atomically-thin platinum shells on gold nanoparticle (NP) cores have been developed through a mild aqueous one-pot synthesis protocol. The loading and homogeneous deposition of Pt on the starch-capped Au NPs can be finely tuned by simply adjusting concentration and the reduction rate of the Pt precursor from 0 to 30 wt% Pt. These Au@Pt NPs have shown impressive catalytic performance for a range of energy relevant reactions due to inherently improved activity of the Pt shells through synergetic interaction with the Au cores.[1,2] Details of the core-shell interface, in particular the atomic-scale and electronic structure of the metal catalyst surface, are crucially important to understand and optimize catalytic properties of the Au@Pt NPs. Characterizing the surface of small nanoparticles with this sensitivity is challenging and most convincingly done by elemental mapping with TEM. However, for Au and Pt, which are very close in atomic mass, lattice parameters and X-ray emission lines, this approach is not sufficient. Here, we have used an array of surface sensitive spectroscopic techniques to characterize the structure of the bimetallic NP surface – specifically, detailed analysis of XPS core-level and valence band photoemission spectra, in combination with elemental analysis using ion scattering spectroscopy (ISS). ISS provides the elemental composition of the surface-exposed atoms, which is very difficult to probe with other techniques. We show that the interface structure involves surface alloying, and sub-surface Pt localization, rather than a simple formation of the Pt overlayer in Au@Pt NPs. Furthermore, time-dependent ISS can potentially be used as a gentle (mild) depth-profiling characterization technique for this kind of core-shell structure and a comparison with a depth-profiling characterization using argon cluster modes will be discussed.

(1) Engelbrekt, C.; Šešelj, N.; Poreddy, R.; Riisager, A.; Ulstrup, J.; Zhang, J. "Atomically thin Pt shells on Au nanoparticle cores: facile synthesis and efficient synergetic catalysis", *J. Mater. Chem. A***2016**, *4* (9), 3278–3286.

(2) Seselj, N.; Engelbrekt, C.; Ding, Y.; Hjuler, H. A. H. A.; Ulstrup, J.; Zhang, J. "Tailored Electron Transfer Pathways in Au$_{\text{core}}$/Pt$_{\text{shell}}$-Graphene Nanocatalysts for Fuel Cells", *Adv. Energy Mater.***2018**, *1702609*, 1702609.

11:20am **AS-ThM-11 Correlating Multiple Data Streams for Valence State Identification in Transition Metal Oxide during XPS Depth Profiling***, **Zhenzhong Yang**, C Wang, M Engelhard, Z Zhu, Y Du,* Pacific Northwest National Laboratory

Transition metal oxides (TMO) of perovskite (ABO$_3$) structures exhibit a broad range of structural, compositional, and functional properties, which can be further tuned or even drastically transformed by means of judicious defect engineering. TMOs have a unique capability to incorporate large amount of oxygen defects owing to the multivalence nature of the transition metal cations, which can be directly probed by XPS. XPS is a surface sensitive technique. In order to study the deeper layers, depth profiling by Ar sputtering is often adopted. However, the sputtering process may change the valence state of the transition metal cations, and thus the data analysis affected by the data acquisition condition can be inaccurate or erroneous.

In this talk, using perovskite SrCrO$_3$ and its reduced structure, SrCrO$_{2.8}$, as model (SCO) materials, I will show how the XPS depth profiling data can reveal the valence state change and redox chemistry occurring in the deeper layers of the SCO thin films. In our experiments, the XPS Cr*2p* spectra suggested that a tensile strain applied by the substrate could stabilize the reduced SrCrO$_{2.8}$ structure near the interface (~10 nm) region. To examine whether the conclusion is correct, we compared SCO samples with different strain states and processing history. By correlating x-ray diffraction (XRD), transmission electron microscopy (TEM), time -of-flight secondary ion mass spectrometry (ToF-SIMS) data and density functional theory calculations, we achieved quantitative agreement and concluded that the Cr 2p spectra were not affected by the Ar beam during the XPS depth profiling process.

11:40am **AS-ThM-12 Using Atom Probe Tomography for Three-dimensional Visualization of Sb Segregation in InAs/InAsSb Superlattices***, **Nicole Kotulak**, J Nolde, M Twigg, K Knipling,* U.S. Naval Research Laboratory*; D Lubyshev, J Fastenau, A Liu,* IQE Inc.*; E Aifer,* U.S. Naval Research Laboratory

Developing materials for mid-wavelength infrared (MWIR) photodetectors has been ongoing, with recent focus on structures that can operate at higher temperatures and across a larger portion of the MWIR range. In recent years, InAs/InAsSb strained layer superlattices (SLS) have been extensively studied and shown to achieve these performance parameters, out-performing the incumbent technologies [1]. Over the course of InAs/InAsSb SL development, as well as in similar Sb-containing device structures, it has been observed that Sb does not remain strictly within the intended layer [2-4].

The segregation of non-common-atoms at a growth interface and into the following layer leads to non-abrupt and asymmetric interfaces, which can cause changes to the optoelectronic properties of the SLS, including fundamental parameters such as band gap and effective mass [2,5,6]. For devices that rely on the precise engineering of the optoelectronic properties of the SLS in order to accomplish performance metrics, non-abrupt interfaces can, ultimately, detrimentally affect device performance, impacting suitability for specific tasks and environments [7]. Understanding the layer compositions at a near atomic-scale can enable these non-idealities to be included in bandstructure simulations to enable device design and optimization [8,9].

In this work, we use atom probe tomography (APT) to harvest 3D compositional data in an MWIR nBn T2SL photodetector consisting of 734 periods of alternating InAs and InAsSb, of which 31 total periods were analyzed. The resulting analysis shows a non-negligible concentration of Sb in the InAs layers, as well as a below-target Sb concentration in the InAsSb layers. While the background concentration of Sb stays consistent as growth of the T2SL progresses, there is an observable increase in the peak Sb concentration from the earliest-grown periods analyzed to the last-grown. These profiles demonstrate corroboration of a non-binary Sb profile observed using complementary techniques, and serve to assist in improving models of Sb-containing SLS for the development of high performance photodetectors.

[1] D. Z. Ting, et al., IEEE Photonics Journal 10, 6804106 (2018).

[2] J. Steinshnider, et al., Phys Rev Lett 85, 2953–2956 (2000).

[3] H. Haugan, et al., J Cryst Growth 436, 134–137 (2016).

[4] K. Kanedy, et al., Appl. Phys. Lett. 112, 042105 (2018).

[5] M. W. Wang, et al., Appl. Phys. Lett. 66, 2981 (1995).

[6] S. B. Rejeb, et al., J Phys D: Appl. Phys 43, 325102 (2010).

[7] K. Shiralagi, et al., J of Elec Materi 26, 1417–1421 (1997).

[8] X. Lü, et al., Appl. Phys. Lett. 104, 232106 (2014).

[9] F. Szmulowicz, et al. Phys. Rev. B, 69, 155321 (2004).

12:00pm **AS-ThM-13 Multi-technique Surface Analysis of Graphenes***,* ***Kateryna Artyushkova***, Physical Electronics and University of New Mexico*; B Schmidt, J Mann, A Ellsworth, J Newman,* Physical Electronics

Several techniques currently being used to determine the thickness of graphene films include optical contrast, Raman and scanning probe microscopy. These methods provide accurate information on thickness but limited information on other important parameters as chemical purity, homogeneity of coverage and defect density. Surface analytical techniques, such as X-ray Photoelectron Spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS), have the potential to fill this gap.

Surface analysis of graphene poses multiple challenges. The thickness of single-layered graphene is on the order of 0.4 nm, while even the most surface-sensitive spectroscopic techniques have on the order of 1-5 nm sampling depth. The surface carbon contamination due to adventitious carbon adds another level of complexity in trying to understand graphene chemistry and homogeneity accurately.

In this report, we will present an analysis of commercially available graphene samples prepared on several types of substrates, such as SiO2 and PET. The chemical structure and thickness of graphene samples were studied by a combination of XPS and TOF-SIMS depth profiling and angle-resolved XPS. The challenges and successes of this multi-technique analysis of graphene will be discussed.

Chemical Analysis and Imaging Interfaces Focus Topic
Room A120-121 - Session CA+2D+AS+BI+NS-ThM

Chemical Analysis and Imaging of Liquid/Vapor/Solid Interfaces II

Moderators: Utkur Mirsaidov, National University of Singapore, Xiao-Ying Yu, Pacific Northwest National Laboratory

8:00am **CA+2D+AS+BI+NS-ThM-1 From Surfaces to Solid-Gas and Solid-liquid Interfaces: Ambient Pressure XPS and Beyond***,* ***Miquel B. Salmeron,*** Lawrence Berkeley Lab, University of California, Berkeley **INVITED**

The rapidly increasing field of surfaces under ambient conditions of temperature and pressure, in gas and liquid environments, reflects the importance of understanding surface properties in conditions closer to practical situations. A lot of progress has been made in the last two decades, enabled by the emergence of a number of new techniques, both spectroscopy and microscopy, that can deliver atomic scale information with the required surface/interface sensitivity. I will present recent advances with examples that illustrate the novel understanding derived from the use of new techniques. One in the gas–solid interface where two important barriers have been bridged: the pressure gap, and the temperature gap. These gaps are very important when dealing with weakly bound molecules, where only in the presence of gas at a suitable pressure, or at low temperatures, a non-negligible coverage of adsorbed molecules can be achieved. The temperature gap manifests also in the removal of kinetic barriers. By bridging these two gaps a host of new interface structures have been unveiled that bring new understanding to catalytic phenomena. This will be illustrated with the examples of Cu and CuCo alloys in the presence of CO. In the case of solid-liquid interfaces, the introduction of new methods using well established x-ray spectroscopies is opening the way to the study of the important electrical double layer structure as a function of applied bias, as I will illustrate with the application of X-Ray absorption and IR to sulfuric acid-Pt and Ammonium Sulfate-graphene interfaces.

8:40am **CA+2D+AS+BI+NS-ThM-3 Probing Solid-liquid Interfaces with Tender X-rays***,* ***Zbynek Novotny****, N Comini, B Tobler,* University of Zuerich, Switzerland*; D Aegerter, E Fabbri,* Paul Sherrer Institute, Switzerland*; U Maier,* Ferrovac GmbH, Switzerland*; L Artiglia, J Raabe, T Huthwelker,* Paul Sherrer Institute, Switzerland*; J Osterwalder,* University of Zuerich, Switzerland

Many important chemical and biological processes occur at the interface between a solid and a liquid, which is difficult to access for chemical analysis. The large inelastic scattering cross section of electrons in the condensed matter makes X-ray photoelectron spectroscopy (XPS) highly surface sensitive but less sensitive to buried interfaces. This limitation can be overcome by stabilizing an ultrathin layer of liquid with a thickness in the order of a few tens of nanometres and by employing tender X-rays (photon energy ranging between 2-8 keV) that can be used to probe the buried solid-liquid interface. We have recently built and commissioned a new instrument at the Swiss Light Source that combines ambient-pressure XPS with in-situ electrochemistry. With this new setup, we can stabilize a thin liquid layer on a solid surface by a dip&pull method [1], and by using tender X-rays (2-8 keV) from the Phoenix beamline, we can probe the properties and chemistry at the solid-liquid and liquid-gas interface while having a potential control over the ultrathin electrolyte film. The capabilities of this new instrument were demonstrated during the first commissioning beamtime, where we stabilized a thin electrolyte layer (0.1 M KOH) over the Ir(001) electrode. The dip&pull technique was used for the first time using well-defined single-crystalline surfaces (see Supplementary document). Core-level binding energy shifts following the applied potential were observed for species located within the electrolyte film. This included the oxygen 1s level from liquid water, potassium, and, interestingly, also an adventitious carbon species, while the interface was carbon-free. We will present the results from the first commissioning beamtime and outline the future directions we are going to pursue using this new instrument.

[1] S. Axnanda, E. J. Crumlin et al., Sci. Rep. 5, 09788 (2014).

9:00am **CA+2D+AS+BI+NS-ThM-4 X-ray Photoelectron Spectroscopy Insight into X-ray Induced Radiolysis at Heterogenous Liquid Electrolyte Interface***,* ***Christopher Arble,*** National Institute of Standards and Technology (NIST)*; H Guo,* Southeast University, China*; E Strelcov, B Hoskins,* National Institute of Standards and Technology (NIST)*; M Amati, P Zeller, L Gregoratti,* Elettra-Sincrotrone Trieste, Italy*; A Kolmakov,* National Institute of Standards and Technology (NIST)

Assessing chemical processes of electrolyte interfaces under operando conditions is an aspirational goal of great importance to many industrial applications[1] that remains technically challenging to investigate. XPS is a powerful characterization tool that can probe elemental and chemical information of atoms with nanoscale depth sensitivity but has traditionally been restricted to UHV conditions. There has been a concerted effort to enable quantitative in-situ measurements of gas and liquid interfaces under realistic environments.[2-4] Recently, advances in 2D materials, i.e., graphene, have been utilized to probe heterogenous interfaces through molecularly impermeable, electron transparent membranes to maintain UHV pressure in the analysis chamber.[5]

Herein we apply photoemission spectromicroscopy to study the electrochemical dynamics of an array of several thousand individual electrolyte cells encapsulated with electron transparent bilayer graphene.[6] We monitored the chemical speciation at the electrode- aqueous $CuSO_4$ electrolyte interface as a function of potential. During the electrochemical experiments, the effects of irradiation upon the solution were observed to influence the system, and spectral deconvolution identified oxidized species of copper and oxygen as well as reduced states of sulfur that were connected to reaction pathways tied with radiolysis. Corresponding SEM images and subsequent EDS spectral maps display spatially confided irradiated byproducts which can be associated with the species observed in with XPS.

Observations of XPS spectroscopic regions in the system were taken at varied X-ray dosages to probe the impacts of radiolysis on the liquid solution concerning the spectroscopic observation of electrochemical deposition of Cu. This experimental methodology imparts a greater understanding of the influence of X-ray induced water radiolysis processes towards the quantification of the electrode/electrolyte interfaces and the underlying dosages necessary for artifact-free data acquisition in condensed media.

References:

1. Saveant, J., *Chemical Reviews* **2008,** 108, (7), 2348-2378
2. Siegbahn, H., *J. Phys. Chem.* **1985,** 89, (6), 897-909
3. Salmeron, M.; Schlögl, R., *Surf. Sci. Rep.* **2008**, 63, (4), 169-199
4. Starr, D.; et al., *Chem. Soc. Rev.* **2013**, 42, (13), 5833-5857
5. Kraus, J.; et al., *Nanoscale* **2014** 6, (23), 14394-14403
6. Yulaev, A.; et al., *ACS Appl. Mater. Interfaces* **2017**, 9, (31) 26492-26502

9:20am **CA+2D+AS+BI+NS-ThM-5 Theoretical Investigation of Reactivity at Complex Solid-Liquid Interfaces***, **Roger Rousseau**,* Pacific Northwest National Laboratory **INVITED**

Contrary to solid/gas interfaces, in solid/liquid interfaces the molecules in the liquid can be organized such that those near the surface are appreciably different from the bulk. This can be impacted by: the composition of the liquid phase, the size shape and loading of nanoparticles and the hydro/lypophilicity of the support. In this talk. we will outline the findings from our ongoing studies of both thermal and electrochemically driven hydrogenation of organic molecules. We will present both classical and ab into molecular dynamics calculations that simulate the structure and composition within the double both at the support as well as on surface of catalytic nanoparticles. The calculations explicitly identify the different roles of entropy and binding energy on the activity and selectivity of solution phase hydrogenation. A first example [1] shows how phenol/water mixtures behave on hydrophilic and lipophilic surfaces, and provides a possible explanation as to why a higher phenol hydrogenation conversion is observed [2] on Pd catalysts on hydrophilic surfaces than on lipophilic surfaces. We show how reaction rates can be manipulated by changing the concentration of phenol adjacent to the catalysts through modification of the degree of support hydrophilicity, size and loading of nanoparticles, and temperature. In a second example [3], we simulate the speciation on a Au and graphitic carbon cathodic surface of a complex solvent mixture containing organics, salts, acids, as a function of cathode charge and temperature. Here we show that the ability to transfer an electron to the organic is governed by the amount of organic in the double layer as well as its orientation with repsect to the electrode surface. While both examples included have been drawn from the upgrading of bio-oil ex pyrolysis, the principles shown are relevant to any application in heterogeneous catalysis with condensed reaction media.

References

1. Cantu DC, Wang YG, Yoon Y, Glezakou VA, Rousseau R, Weber RS. 2016, Catalysis Today, http://dx.doi.org/10.1016/j.cattod.2016.08.025

2. Perez Y, Fajardo M, Corma A. 2011, Catalysis Communications, 12, 1071-1074.

3. Padmaperuma AB, Cantu DC, Yoon Y, Nguyen MT, Wang YG, Glezakou VA, Rousseau R, Lilga MA. Manuscript in preparation, to be submitted.

11:00am **CA+2D+AS+BI+NS-ThM-10 In-situ/Operando Soft X-ray Spectroscopy for Interfacial Characterization of Energy Materials and Devices***, Y Liu, X Feng, **Jinghua Guo**,* Lawrence Berkeley National Laboratory

In-situ/operando soft x-ray spectroscopy offers unique characterization in many important energy materials of energy conversion, energy storage and catalysis in regards to the functionality, complexity of material architecture, chemistry and interactions among constituents within.

It has been found that the microstructure and composition of materials as well as the microstructure evolution process have a great influence on performances in a variety of fields, e.g., energy conversion and energy storage materials, chemical and catalytic processes. In-situ/operando x-ray spectra characterization technique offers an opportunity to uncover the phase conversion, chemical environment of elements and other critical information of solid/liquid interfaces in real time. We will present soft x-ray spectroscopy characterization techniques, e.g. soft x-ray absorption spectroscopy (XAS) and resonant inelastic soft x-ray scattering (RIXS), and the development of in situ/operando capabilities for the characterization of interfacial phenomena in energy materials and devices.

A number of the experimental studies, which revealed the catalytic and electrochemical reactions in real time, will be presented, e.g. solid (metal film)/liquid (water) electrochemical interface, Mg-ion batteries, and Li-S batteries [1-5]. The experimental results demonstrate that in-situ/operando soft x-ray spectroscopy characterization provides the unique information for understanding the real reaction mechanism.

References:

1. "Mg deposition observed by in situ electrochemical Mg K-edge X-ray absorption spectroscopy", T. S. Arthur, P.-A. Glans, M. Matsui, R. Zhang, B. Ma, J.-H. Guo, Electrochem. Commun. **24**, 43 (2012)

2. "The structure of interfacial water on gold electrodes studied by x-ray absorption spectroscopy", J. J. Velasco-Velez, C. H. Wu, T. A. Pascal, L. F. Wan, J.-H. Guo, D. Prendergast and M. Salmeron, Science **346**, 831 (2014)

3. "Nucleophilic substitution between polysulfides and binders unexpectedly stabilizing lithium sulfur battery", M. Ling, L. Zhang, T. Zheng, J. Feng, J.-H. Guo, L. Mai, G. Liu, Nano Energy **38**, 82 (2017).

4. "Interfacial insights from operando sXAS/TEM for magnesium metal deposition with borohydride electrolytes", T. Arthur, P.-A. Glans, N. Singh, O. Tutusaus, K. Nie, Y.-S. Liu, F. Mizuno, J.-H. Guo, D. H. Alsem, N. Salmon, R. Mohtadi, Chem. Mater. **29**, 7183 (2017).

"Revealing the Electrochemical Charging Mechanism of Nanosized Li2S by in Situ and Operando X-ray Absorption Spectroscopy", L. Zhang, D. Sun, J. Feng, E. Cairns, J.-H. Guo, Nano Lett. **17**, 5084 (2017).

11:20am **CA+2D+AS+BI+NS-ThM-11 The Importance of Amino Acid Adsorption on Polymer Surfaces in *P. Aeruginosa* Biofilm Formation***, **Olutoba Sanni**,* University of Nottingham, UK

High throughput materials discovery screens have revealed polymers that reduce bacterial surface colonization which have progressed to currently ongoing clinical trials [Hook *et al*. Nature Biotech 2012]. These novel poly (meth)acrylate coatings reduced biofilm formation by *Pseudomonas aeruginosa, Staphylococcus aureus* and *Escherichia coli* in laboratory cultures *in vitro* and *in vivo* in a mouse foreign body infection model. These coatings are known to function by preventing biofilm formation, however why the bacterial cells respond in this way to these polymers has yet to be elucidated. The initial interaction between bacteria and surfaces has been identified as a key determining factor when bacteria decide to either irreversibly attach and colonise a surface or not.

The exposure of most materials to biological milieu is accompanied by adsorption of biomolecules. In protein containing media there is a strong relationship between the adsorbed protein layer formed on materials and mammalian cell attachment. However, in protein-free media such as used by Hook et al., this cannot be a contributor to early bacterial cell attachment. Consequently, here we carry out careful surface chemical analysis on two polymers known to exhibit drastically different biofilm formation in a standard protein-free, amino acid containing bacterial culture medium (RPMI).

Time of flight secondary ion mass spectrometry (ToF-SIMS) and X-ray photoelectron spectroscopy (XPS) analysis determined that high amino acid adsorption correlates with the surface exhibiting low *P. aeruginosa* colonisation. A total of 10 peaks characteristic of specific amino acids were identified by ToF-SIMS to be adsorbed on polymer. We successfully fitted the Freundlich and Langmuir adsorption isotherm models from which we determined adsorption capacity of polymers, calculated the on/off rate of amino acid adsorption on both anti-biofilm and pro-biofilm surfaces. With XPS, the overlayer coverage of amino acids on the polymer surface was established to be approximately 0.2 nm.

The study was extended to quantify in high throughput manner the adsorption of amino acids from RPMI media onto surfaces of 288 polymer materials printed onto a microarray. Ion fragments generated from ToF-SIMS were used to produce a regression model from which we identified polymers with cyclic moieties as major promoters of amino acid adsorption.

This is the first report suggesting adsorbed amino acids or other adsorbed nutrients may correlate with the biofilm formation tendency of materials.

Frontiers of New Light Sources Applied to Materials, Interfaces, and Processing Focus Topic
Room A124-125 - Session LS+AS+SS-ThM

Operando Methods for Unraveling Fundamental Mechanisms in Devices Towards Renewable Energies

Moderator: Olivier Renault, CEA-University Grenoble Alps, France

8:00am **LS+AS+SS-ThM-1 X-Ray Insight into Fuel Cell Catalysis: Operando Studies of Model Surfaces and Working Devices***, **Jakub Drnec**, I Martens,* European Synchrotron Radiation Facility, France*; T Fuchs,* University of Kiel, Germany*; T Wiegmann,* European Synchrotron Radiation Facility, Germany*; A Vamvakeros,* Finden Ltd., UK*; R Chattot,* European Synchrotron Radiation Facility, France*; O Magnussen,* University of Kiel, Germany **INVITED**

Complete physico-chemical operando characterization of electrochemical devices in whole, or it's constituent materials separately, is necessary to guide the development and to improve the performance. High brilliance synchrotron X-ray sources play a crucial role in this respect as they act as a probe with relatively high penetration power and low damage potential. In this contribution the new possibilities of using using high energy, high intensity X-rays to probe model fuel cell catalysts and energy conversion devices will be presented.

HESXRD (High Energy Surface X-ray Diffraction) [1] and TDS (Transmission Surface Diffraction) [2] provide ideal tools to study structural changes during reaction conditions on single crystal model electrodes. The main advantage of both techniques is the possibility to follow the structural changes precisely with atomic resolution. While HESXRD is ideally used to determine exact atomic position, the TSD is easier to use and allows studies with high spatial resolution. For example, HESXRD can be used to follow the atomic movement of Pt atoms during electrochemical oxidation and dissolution with very high precision, explaining the different catalyst degradation behaviors and suggesting possible routes to improve its durability [3-4]. The TSD is an excellent tool to study advanced 2D catalysts.

To study fuel cells or batteries as a whole, elastic scattering techniques, such as WAXS and SAXS, can be employed as they can provide important complementary information to more standard X-ray imaging and tomography. The advantage is that the chemical contrast and sensitivity at atomic and nm scales is superior. Coupling these technique with the tomographic reconstruction (XRD-CT and SAXS-CT) is much less common as it requires bright synchrotron sources and advanced instrumentation, but allows 3D imaging of operational devices with unprecedented chemical sensitivity. This can be demonstrated on imaging of standard 5 cm^2 fuel cells during operation. The change in morphology and atomic arrangement of the catalysts, PEM hydration and water distribution can be followed in one experiment as a function of operating conditions. Furthermore, the fundamental processes leading to the catalyst aging can be assessed with high temporal and spatial resolution. These advanced scattering techniques open a door to holistic investigations of operational devices, which are needed to successfully incorporate new materials at the device level.

[1] J. Gustafson et al., Science 343, 758 (2014)

[2] F. Reikowski et al., J. Phys. Chem. Lett., 5, 1067-1071 (2017)

[3] J. Drnec et al, Electrochim. Acta, 224 (2017),

[4] Chattot et al., Nature Materials, 17(2018)

8:40am **LS+AS+SS-ThM-3 Multi-scale Operando X-ray Tomography of Solid-state Li Battery Electrolytes at Elevated Temperatures and Pressures*, Natalie Seitzman,*** Colorado School of Mines*; J Nelson Weker,* SLAC National Accelerator Laboratory*; M Al-Jassim,* National Renewable Energy Laboratory*; S Pylypenko,* Colorado School of Mines

Solid state Li ion conductors are next-generation battery technologies that reap the capacitive benefits of Li metal anodes while mechanically resisting the Li interface evolution and thus prolonging lifetime. Additionally, they are not flammable, offering greater safety than liquid counterparts. However, interface evolution and Li protrusions are observed in solid state batteries despite the mechanical resistance.[1,2] There is debate as to whether these protrusions nucleate at the Li anode or within the ceramic electrolyte, and there are several factors that affect these protrusions including electrolyte density, pre-existing defects, anode/electrolyte interfacial contact, and imperfect electronic insulation within the electrolyte.[3] Understanding the influence of these variables is greatly enhanced by directly imaging the interior of the ceramic at multiple scales in conjunction with electrochemical experiments.

This talk addresses the contribution of electrolyte density and defects, interfacial contact, and conductivity to structural changes in β-Li_3PS_4 (LPS) ceramic electrolyte in operating cells via 3D X-ray imaging with sub-micron resolution. Cells of Li, LPS, and a blocking contact are constructed and studied *in operando* at 200 psi and 70˚C. Because electrolyte density and initial defects depend on the composition and synthesis of the ceramic conductor, two syntheses of LPS with different particle sizes are compared. Also, pressure is a key parameter in the quality and stability of interfacial contact while temperature affects both the ionic and electronic conductivity of the ceramic.

Synchrotron micro-tomography is combined with synchrotron transmission x-ray microscopy to study the cells with spatial resolution in the hundreds of nanometers and tens of nanometers. Image analysis of these data has identified sites of Li microstructure growth[4] and now isolates variable-dependent trends such as pressure-dependent void formation in the Li anode. Linking structural changes observed *in operando* to these factors that contribute to Li evolution will guide the design of robust ceramic electrolytes with improved performance and safety.

1. L. Porz, T. Swamy, B. W. Sheldon, D. Rettenwander, T. Frömling, H. L. Thaman, S. Berendts, R. Uecker, W. C. Carter, and Y.-M. Chiang, *Adv. Energy Mater.*, **7**, 1701003 (2017).

2. E. J. Cheng, A. Sharafi, and J. Sakamoto, *Electrochim. Acta*, **223**, 85–91 (2017).

3. F. Han, A. S. Westover, J. Yue, X. Fan, F. Wang, M. Chi, D. N. Leonard, N. J. Dudney, H. Wang, and C. Wang, *Nat. Energy* (2019).

4. N. Seitzman, H. Guthrey, D. B. Sulas, H. A. S. Platt, M. Al-Jassim, and S. Pylypenko, *J. Electrochem. Soc.*, **165**, 3732–3737 (2018).

9:00am **LS+AS+SS-ThM-4 Correlating the Atomic and Electronic Structure in the Formation 2DEGs in Complex Oxides*, Jessica McChesney,*** *X Yan, F Wrobel, H Hong, D Fong,* Argonne National Laboratory

Using a multimodal approach, we investigate the interplay of the atomic and electronic structure of the formation of 2-D electron gas (2DEG) in complex oxide systems. Using hybrid molecular beam epitaxy for synthesis and in-situ synchrotron x-ray scattering atomic precision of the growth is obtained. The electronic structure then characterized via a combination of resonant soft x-ray angle-resolved photoemission and core level spectroscopy and compared with transport measurements.

9:20am **LS+AS+SS-ThM-5 Uncover the Mystery of Oxygen Chemistry in Batteries through High-Efficiency mRIXS and Theory*, Wanli Yang,*** Lawrence Berkeley National Laboratory **INVITED**

Energy storage through electrochemical devices (batteries) is under pressure to be greatly improved for today's sustainable energy applications, especially the electric vehicles and power grid using renewable energy sources. A battery utilizes transition-metal (TM) oxides as one of the critical electrodes, the positive electrode, which is often the bottleneck of the energy density. In general, the operation of battery cycling is based on reduction and oxidation (Redox) reactions of TMs and a recently proposed oxygen, which involve the changes on the electron occupation numbers in TM-*3d* and O-*2p* states, as well as the evolution of the electronic configuration. However, technical challenges are formidable on probing these states directly, especially for the unconventional oxygen redox states.

This presentation will start with a brief introduction of several needs and grand challenges of battery devices related with oxygen states, which is followed by soft X-ray spectroscopic experiments for providing relevant information. The focus of this presentation is on an active debate of the oxygen states in charged electrodes. We will explain the limitations on conventional soft X-ray absorption spectroscopy (sXAS) for characterizing the important oxygen states, then showcases the power of full energy-range mapping of resonant inelastic X-ray scattering (mRIXS) for clarifying the oxygen redox behaviors in batteries.

We show that mRIXS provides the ultimate probe of the intrinsic oxygen redox reactions in the lattice of battery electrodes [1], which is associated with transition-metal configurations [2]. These spectroscopic results could be quantified to decipher the electrochemical capacity [3], providing both the rationality of the device performance and evidences for understanding the fundamental mechanism of electrochemical materials for energy applications. Furthermore, the mRIXS results indicate a universal driving force of the oxygen redox reactions [4], which could be tackled through combined studies of mRIXS and theoretical calculations [5]. We show that such a spectroscopic and theoretical collaboration could deliver unprecedented information for both fundamental understanding and practical optimization on grand challenges in developing high-performance battery devices.

[1] Gent et al., Nat Comm 8, 2091 (2017)

[2] Xu et al., Nat Comm 9, 947 (2018)

[3] Dai et al., Joule 3, 518 (2019)

[4] Yang & Devereaux, J. Power Sources 389, 188 (2018)

[5] Zhuo et al., JPCL 9, 6378 (2018)

Magnetic Interfaces and Nanostructures Division
Room A210 - Session MI+2D+AS+EM-ThM

Novel Magnetic Materials and Device Concept for Energy efficient Information Processing and Storage

Moderators: Mikel B. Holcomb, West Virginia University, Markus Donath, Muenster University, Germany

8:00am **MI+2D+AS+EM-ThM-1 Using Novel Magnonic Device Concepts for Efficient Information Processing*, Burkard Hillebrands,*** Technical University Kaiserslautern, Germany **INVITED**

In the field of magnonics, wave-based logic devices are constructed and studied based on the utilization of spin waves and their quanta - magnons. The field is developing rapidly due to its potential to implement innovative ways of data processing as a CMOS complementary technology. Basic building blocks of magnonics have already been realized. Examples are linear and nonlinear spin-wave waveguide structures, magnonic logic, as well as magnonic amplifiers such as the magnon transistor and parametric amplification.

In this talk, I will give an overview about the fundamentals and the current trends in magnonics. One topic is the realization of new functionalities and devices by using novel concepts borrowed from integrated optics and combining them with the specific advantages found in magnetic systems. Examples are directional couplers and quantum-classical analogy devices, such as a magnonic Stimulated Raman Adiabatic Passage (STIRAP) device.

Another important direction is to use fundamentally new macroscopic quantum phenomena such as a Bose-Einstein condensate (BEC) at room temperature as a novel approach in the field of information processing technology. Very promising is the use of magnon supercurrents driven by a phase gradient in the magnon BEC. I will demonstrate evidence of the formation of a magnon supercurrent along with second magnonic sound, and its spatiotemporal behavior, which is revealed by means of time- and wavevector-resolved Brillouin light scattering (BLS) spectroscopy. I will conclude with an outlook.

8:40am **MI+2D+AS+EM-ThM-3 Spin-Polarized Scanning Tunneling Microscopy of <10 nm Skyrmions in SrIrO3/SrRuO3 Bilayers*, Joseph Corbett,*** *J Rowland, A Ahmed, J Repicky,* The Ohio State University*; K Meng,* The Ohio State Univesity*; F Yang, M Randeria, J Gupta,* The Ohio State University

We imaged isolated <10 nm sized skyrmions in $SrIrO_3$ on $SrRuO_3$ by spin-polarized scanning tunneling microscopy. We fabricated bilayers of 2 unit cells of $SrIrO_3$ atop of 10 unit cells of $SrRuO_3$ via off-axis sputtering. This thickness combination was selected because it showed a strong topological hall signal. We observed a granular morphology of $SrIrO_3$ mounds with rare patches of exposed $SrRuO_3$. We can distinguish $SrIrO_3$ from $SrRuO_3$ by scanning tunneling spectroscopy where, $SrIrO_3$ grains show a gap-like feature, while $SrRuO_3$ have states near the Fermi level. The height histogram of the observed granular structures is consistent with an average of 2 unit cells of $SrIrO_3$. The grains of the $SrIrO_3$ appear to act as a nucleation for skyrmion formation. Similarly, we've imaged skyrmions under applied +/- 1 T fields demonstrating their magnetic character by observing an inversion in magnetic contrast. We found that the number of $SrIrO_3$ unit cells did not determine skyrmion formation, but the size of the skymrion was linked to the grain size, i.e. the skyrmion formed roughly the size of the grain. Furthermore, we've been able to manipulate the skyrmions by utilizing the influence of the tip. On-going investigations into the mechanism of the magnetic manipulation of the skyrmion are underway, as well theoretical modeling of the isolated skyrmion to ascertain the local Dzyaloshinskii-Moriya interaction constant.

9:00am **MI+2D+AS+EM-ThM-4 Relieving YIG from its Substrate Constraints - YIG Resonators on Various Crystalline Substrate Materials*, Georg Schmidt,*** Martin-Luther-Universität Halle-Wittenberg, Germany **INVITED**

We have recently demonstrated the fabrication of free-standing 3D yttrium iron garnet (YIG) magnon nano-resonators with very low damping [1]. At first the resonators were fabricated on gallium gadolinium garnet (GGG) substrates which are most suitable for epitaxial deposition of YIG. The process involves room temperature deposition and subsequent annealing. Transmission electron microscopy investigation of the bridge-like structures shows that the span of the bridge is almost monocrystalline while some defects nucleate at the transitions from the span to the posts of the bridge which are epitaxially bound to the substrate. This suggests that the quality of the span may only indirectly depend on the quality of the feet, the latter being largely determined by the lattice matching of the substrate material to the YIG. Being able to grow YIG structures on substrate materials other than GGG would not only be interesting because of availability and price but also because the high frequency properties of GGG are less than ideal while other materials like MgO or Sapphire would be preferred for high frequency applications. We have fabricated YIG bridges on various substrate materials including yttrium aluminium garnet (YAG), MgO, and sapphire. In most cases we achieve high crystalline quality of the span even for non-matching substrates. For some of the materials time resolved magneto optical Kerr microscopy even reveals magnon resonances with reasonable linewidth.

[1] F. Heyroth et al. cond-mat.1802.03176

9:40am **MI+2D+AS+EM-ThM-6 Magnetic Textures in Chiral Magnet MnGe Observed with SP-STM*, Jacob Repicky,*** *J Corbett, T Liu, R Bennett, A Ahmed,* The Ohio State University*; J Guerrero-Sanchez,* National Autonomous University of Mexico*; R Kawakami, J Gupta,* The Ohio State University

Materials with non-centrosymmetric crystal structures can host helical spin states including magnetic skyrmions. Bulk MnGe hosts a short period magnetic state (3 nm), whose structure depends strongly on atomic lattice strain, and shows a large emergent transport signature associated with the skyrmion phase. Here, we use low-temperature (5 K) spin-polarized scanning tunneling microscopy (SP-STM) to image the magnetic textures in MnGe thin films grown via molecular beam epitaxy and study the influence of the surface on those textures. Most microscopic locations show a spin spiral phase with a 6-8 nm period and a propagation direction that is influenced by step edges and surface termination. We also report the presence of isolated target skyrmions which have a triangular shape that appears to be set by the in-plane lattice vectors, and a core size of approximately 15 nm. We observe the target state is significantly more sensitive to magnetic fields than the spiral phase, and that local voltage and current pulses with the STM tip imply the texture can be 'switched' between states with different topological charge. Detailed analysis of atomic resolution STM images is used to probe the role of small lattice strain on the distinct textures. To fully understand the magnetic textures in MnGe we will expand this study by investigating films of different thicknesses to vary the magnetic anisotropy and strain.

Funding for this research was provided by the Defense Advanced Research Projects Agency Grant No. 18AP00008

11:00am **MI+2D+AS+EM-ThM-10 Dzyaloshinskii-Moriya Interaction in Magnetic Multilayers*, Hans Nembach,*** National Institute of Sandards and Technology (NIST) **INVITED**

The Dzyaloshinskii-Moriya Interaction (DMI) gives rise to chiral magnetic structures, which include chiral spin-chains and skyrmions. The latter have recently received much attention, especially for their potential application for magnetic data storage. Each skyrmion would represent a bit and would be moved along a racetrack. DMI requires broken inversion symmetry and can exist in the bulk as well as at interfaces, for example at interfaces between a ferromagnet and a material with large spin-orbit coupling like heavy metals. More recently it has been shown that interfacial DMI can also exist at interfaces with graphene and oxides.

We use Brillouin Light Scattering spectroscopy (BLS) to determine the DMI from the non-reciprocal frequency-shift Damon-Eshbach spin-waves. In order to gain deeper insight into the underlying physics of DMI, we prepared several sample series to study different aspects of the DMI. First, we prepared two samples series to study the relationship between the DMI and the Heisenberg exchange. One series was a $Ni_{80}Fe_{20}$ thickness series on a Pt layer and for the other series we introduced a Cu dusting layer at the interface between a CoFeB layer and Pt to disrupt the Heisenberg exchange directly at the interface. For both sample series, we found that the Heisenberg exchange and the DMI are proportional to each other as it has been predicted by theory. Next, we prepared a $Cu/Co_{90}Fe_{10}$ and a $Pt/Co_{90}Fe_{10}$ sample series, which were in-situ oxidized for different times and subsequently capped to prevent any further oxidation. Density functional theory calculations have shown that the hybridization and the associated charge transfer is important for the DMI and that interfaces with an oxide can have DMI. Our BLS measurements showed that oxide interfaces have DMI. Moreover, we showed that the spectroscopic splitting factor g, which we determined with ferromagnetic resonance spectroscopic, is correlated to the DMI. This is an indirect confirmation of the theory predictions regarding the role of hybridization and charge transfer.

So far, most work on DMI has been carried out for highly symmetric interfaces. Low symmetry systems can have anisotropic DMI and can potentially support anti-skyrmions. We prepared a Pt/Fe(110) sample and found that the DMI is anisotropic with the strongest DMI along the [001] direction, which coincides with the magnetic easy axis.

Finally, we studied the impact of He^+ ion irradiation on DMI for the Ta/CoFeB/Pt system. We found that the DMI increases with the dose before it drops for the highest does. This is in contrast to the perpendicular anisotropy, which continuously decreases with ion-irradiation.

11:40am **MI+2D+AS+EM-ThM-12 Transport in Goniopolar and (pxn) Metals*, Joseph Heremans*, *B He, L Zheng, Y Wang, M Arguilla, N Cultrara, M Scudder, J Goldberger, W Windl,* The Ohio State University **INVITED**

semiconductors that have *p*-type conduction along some crystallographic directions and *n*-type conduction along others due to a particular topology of their Fermi surface. The electrical and thermoelectric transport of one member of this class, $NaSn_2As_2$, will be presented. A second class of materials have similar transport properties due to different mechanisms: some, like Be and Cd, have Fermi surfaces that contain both electron and hole pockets that have partial thermopowers of opposite polarities, but very anisotropic mobilities, so that one carrier type dominates the total thermopower in one direction, and the other carrier type dominates the thermopower in the other direction. A new member of this class, the semimetal bismuth doped p-type with Sn, will be described in this talks as well. In practice, a third class of artificial materials made of separate layers of p-type and of n-type semiconductors can be made to have a similar behavior in transport as well; the last two classes are called (pxn)-materials.

The electrical conductivity and thermopower tensors in goniopolar and (pxn) materials can be made to have off-diagonal components, which cause exciting new properties like zero-field Hall and Nernst-Ettingshausen effects. These materials can be used in single-crystal transverse thermoelectrics.

[1] He, B. et al , *Nat. Mater.* (published online doi.org/10.1038/s41563-019-0309, 2019)

[2] Zhou, C. et al. *Phys. Rev. Lett.* **110**, 227701 (2013).

Surface Science Division
Room A220-221 - Session SS+AS+HC+TL-ThM
Surface Science of Energy Conversion and Storage

Moderators: Steven L. Tait, Indiana University, Francisco Zaera, University of California, Riverside

8:00am **SS+AS+HC+TL-ThM-1 Chemical and Electrochemical Stability of Perovskite Oxide Surfaces in Energy Conversion: Mechanisms and Improvements*, Bilge Yildiz,*** Massachusetts Institute of Technology **INVITED**

A broad range of highly active doped ternary oxides, including perovskites, are desirable materials in electrochemical energy conversion, catalysis and information processing applications. At elevated temperatures related to synthesis or operation, however, the structure and chemistry of their surfaces can deviate from the bulk. This can give rise to large variations in the kinetics of reactions taking place at their surfaces, including oxygen reduction, oxygen evolution, and splitting of H_2O and CO_2. In particular, aliovalent dopants introduced for improving the electronic and ionic conductivity enrich and phase separate at the surface perovskite oxides. This gives rise to detrimental effects on surface reaction kinetics in energy conversion devices such as fuel cells, electrolyzers and thermochemical H_2O and CO_2 splitting. This talk will have three parts. First, the mechanisms behind such near-surface chemical evolution will be discussed. Second, the dependence of surface chemistry on environmental conditions, including temperature, gas composition, electrochemical potential and crystal orientation will be described. Third, modifications of the surface chemistry that improve electrochemical stability and actvity, designed based on the governing mechanisms, will be presented. Guidelines for enabling high performance perovskite oxides in energy conversion technologies will be presented.

8:40am **SS+AS+HC+TL-ThM-3 Mechanism of Oxygen Reduction Reaction on Nitrogen-doped Carbon Catalysts*, Junji Nakamura,*** University of Tsukuba, Japan

Nitrogen-doped carbon materials are expected to be non-Pt catalysts for oxygen reduction reaction (ORR) in fuel cells. Among several types of nitrogen species in carbon materials, pyridinic nitrogen (nitrogen atom bound to two C atoms) has been found to create ORR active sites in our previous work[1]. We then try to prepare catalytically active carbon surfaces covered with pyridinic nitrogen-containing aromatic molecules with high density. Recently we have reported model catalyst studies using HOPG (highly oriented pyrolytic graphite) electrode covered with pyridinic nitrogen-containing aromatic molecules (dibenz[a,c] acridine (DA) molecule and acridine (Ac)molecule)[2]. The DA molecules form a two-dimensional ordered structure along the direction of the HOPG substrate by self-organization. Adsorbed DA on the HOPG surface shows high ORR activity in terms of specific activity per pyridinic nitrogen and is comparable to that of pyridinic-nitrogen-doped carbon catalysts. We study the mechanism of ORR taking place on the DA/HOPG model catalyst. In acidic reaction conditions, pyridinic nitrogen is protonated to pyridinium nitrogen (NH+) species. It is suggested that the adsorption of oxygen take place on a carbon atom in a DA molecule upon reduction of the NH+ species. Generally, the reduction of NH+ is difficult to proceed thermodynamically at higher potentials above 0 V vs RHE. However, in the presence of oxygen, the reduction of NH+ is possible by an energy gain due to simultaneous adsorption of oxygen. The supplied electron goes to pai system as SOMO electron upon reduction, which is responsible for the adsorption of oxygen. That is, the role of pyridinic nitrogen is to provide SOMO electron upon reduction of NH+ species.

References

Guo D, Shibuya R, Akiba C, Saji S, Kondo T, Nakamura J, (2016). Active sites of nitrogen-doped carbon materials for oxygen reduction reaction clarified using model catalysts. *Science*, 351, 361-365.

Shibuya R, Kondo T, Nakamura J, (2018). Bottom-up design of nitrogen-containing carbon catalysts for the oxygen reduction reaction. *ChemCatChem* doi.org/10.1002/cctc.201701928

9:00am **SS+AS+HC+TL-ThM-4 Copper Corrosion Inhibition Investigated on the Molecular Scale Using APXPS*, Bo-Hong Liu,*** Lawrence Berkeley National Laboratory*; O Karslıoğlu,* Lawrence Berkeley Nationa lLaboratory*; M Salmeron, S Nemšák,* Lawrence Berkeley National Laboratory*; H Bluhm,* Fritz Haber Institute of the Max Planck Society, Germany

Copper has been used in a wide variety of applications. Though relatively inert, it corrodes when in contact with aqueous solutions/water vapor and corroding agents such as chlorine.[1] Benzotriazole (BTA) is a commonly used corrosion inhibitor to protect copper surfaces. A consensus regarding the mechanism of corrosion protection is that BTA complexes with surface copper atoms, resulting in a Cu(I)-BTA protective polymer layer.[2] UHV-based surface science studies clarified the structure of the BTA layer on copper single crystal surfaces at low dosage, as demonstrated by a very recent study combining DFT and spectroscopic techniques;[3] however, the effect of environmental factors could not be well addressed by this approach. Here, we report an Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) study of the influence of water vapor and chlorine on well-defined Cu surfaces. To capture the material complexity of the corrosion phenomenon, we study copper single crystals as well as polycrystalline foils of metallic copper, cuprous oxide and cupric oxide. In this presentation, we will show that the water uptake of copper surfaces under humid condition is strongly influenced by the presence of a BTA layer. Also, a BTA layer blocks chlorine uptake in some conditions. Based on these experimental results, factors that influence the BTA inhibitory effect on copper corrosion are identified.

1. Atlas, D.; Coombs, J.; Zajicek, O. T., THE CORROSION OF COPPER BY CHLORINATED DRINKING WATERS. *Water Research* **1982,***16* (5), 693-698.

2. Finsgar, M.; Milosev, I., Inhibition of copper corrosion by 1,2,3-benzotriazole: A review. *Corrosion Science* **2010,***52* (9), 2737-2749.

3. Gattinoni, C.; Tsaousis, P.; Euaruksakul, C.; Price, R.; Duncan, D. A.; Pascal, T.; Prendergast, D.; Held, G.; Michaelides, A., Adsorption Behavior of Organic Molecules: A Study of Benzotriazole on Cu(111) with Spectroscopic and Theoretical Methods. *Langmuir* **2019,***35* (4), 882-893.

9:20am **SS+AS+HC+TL-ThM-5 Analysis and Deliberate Modification of Electrochemical Interfaces*, Esther Takeuchi*,** *K Takeuchi, A Marschilok,* Stony Brook University **INVITED**

Interfaces in electrochemical energy storage systems are critical in the transport of electrons and ions and are significant factors in electrochemical function, yet remain a challenge to fully understand. In lithium based systems, the interfaces or interphases often form spontaneously due to reactions of the active materials and the electrolytes. The interfaces formed due to these spontaneous reactions may prove beneficial as they provide needed protection inhibiting further and continuous reaction. However, the characteristics of the interface may also contribute to decreased ion transport and the accompanying increased effective resistance.

Conversion-type materials for next generation lithium ion systems are appealing due to the opportunity for multiple electron transfer within one metal center. However, implementation of conversion materials has been hindered by the phase transformations occurring during cycling as well as formation of a resistive solid electrolyte interphase (SEI). This presentation will explore the effective implementation of combinations of characterization techniques including the use of *ex-situ* and *operando* methods to provide insight into the formation, composition and deliberate modification of the SEI.

11:00am **SS+AS+HC+TL-ThM-10 An Investigation on Active Sites of La_2O_3 Catalyst for OCM Reaction: A Combined Study of *in situ* XRD, XPS and Online MS***, **Yong Yang**, C Guan, E Vovk, Z Liu, X Zhou, J Liu, Y Pang,* ShanghaiTech University, China

Oxidative coupling of methane (OCM) is a catalytic partial oxidation process that converts methane directly to valuable C_2 products (ethane and ethylene). Previous results suggested that the bulk structure change of the La_2O_3 catalyst was related to the performance of the reaction. In this work, a designed *in situ* XRD-MS coupled characterization setup coupled with online MS instrument are used for measuring both the reaction products and the bulk structure of the catalyst in real time and under simulated industrial conditions. This allows for the more detailed study in order to relate information from of bulk structure change vs. CO_2 related treatment and quantitative analysis of the reaction products, thus for a further connection and understanding of the conversion rate of CH_4 and the selectivity of C_2. The work presented focused on online characterization of the OCM reaction on La_2O_3 catalyst, covering different parameters including: 1. La_2O_3 pretreatment under different CO_2 concentrations, 2. Consecutive OCM reactions, comparing the behavior of a clean surface La_2O_3 catalyst with a La_2O_3 catalyst after OCM, 3. OCM performed after La_2O_3 has undergone pretreatment with pure CO_2. Results indicate that carbonates formation on La2O3 is two step, surface carbonates formation at below 500°C and bulk formation at 500-700°C. *In situ* TPD performed in a high pressure gas cell (HPGC) and XPS measurement results confirm the above.

The results showed that bulk CO_3^{2-} formation under CO_2 exposure, results in higher light-off temperature of CO_2 and C_2 than the clean surface during OCM reaction. There is carbonate formation on commercial La_2O_3 during OCM reaction and CO_2 desorption after OCM reaction by in situ XRD-MS, and it influences the light-off temperature of CO_2 and C_2 up to 65°C higher than the clean surface. It is proposed that CO_3^{2-} may perform as a catalyst poison in this reaction. This result provides an important insight of the active site for OCM reaction. Based on this result, a brief XPS study of the carbonate free sample surface, which may be only preppared from the HPGC vacuum connected further reveals an oxide feature related with methane activation. Additional DFT calculations based upon the experimental data indicates a carbonation mechanism which occurs in the subsurface, which in turn could be related to La_2O_3 activity.

11:20am **SS+AS+HC+TL-ThM-11 Interaction of Amino Acids on Au(111) as Studied with EC-STM: From Islands to Magic Fingers***, J Phillips, K Boyd, I Baljak, L Harville,* ***Erin Iski,*** University of Tulsa

With growing interest into origin of life studies as well as the advancement of medical research using nanostructured architectures, investigations into amino acid interactions have increased heavily in the field of surface science. Amino acid assembly on metallic surfaces is typically investigated with Scanning Tunneling Microscopy (STM) at low temperatures (LT) and under ultra-high vacuum (UHV), which can achieve the necessary resolution to study detailed molecular interactions and chiral templating. However, in only studying these systems at LT and UHV, results often tend to be uncertain when moving to more relevant temperatures and pressures. This investigation focuses on the Electrochemical STM (EC-STM) study of five simple amino acids (L-Valine, L-threonine, L-Isoleucine, L-Phenylalanine, and L-Tyrosine) as well as two modifications of a single amino acid (L-Isoleucine Ethyl Ester and N-Boc-L-Isoleucine), and the means by which these molecules interact with a Au(111) surface. Using EC-STM under relevant experimental conditions, the amino acids were shown to have a considerable interaction with the underlying surface. In some cases, the amino acids trapped diffusing adatoms to form Au islands and in other cases, they assisted in the formation of magic gold fingers. Importantly, these findings have also been observed under UHV conditions, but this is the first demonstration of the correlation *in situ* and was controlled via an applied external potential. Results indicate that an increase in the molecular weight of the amino acid had a subsequent increase in the area of the islands formed. Furthermore, by shifting from a nonpolar to polar side chain, island area also increased. By analyzing the results gathered via EC-STM at ambient conditions, fundamental insight can be gained into not only the behavior of these amino acids with varied side chains and the underlying surface, but also into the relevance of LT-UHV STM data as it compares to data taken in more realistic scenarios.

11:40am **SS+AS+HC+TL-ThM-12 Deposition and Structure of MoO_3 Clusters on Anatase TiO_2 (101)***,* ***Nassar Doudin****, Z Dohnálek,* Pacific Northwest National Laboratory

Oxide clusters supported on metal oxide substrates are of great interest due to their importance in heterogeneous catalysis [1]. The nature and strength of the interactions between the metal oxide clusters and the support materials not only govern their structure and stability but also control the energetics of elementary steps that are critical for the overall activity [1]. Understanding the nature of the interactions is therefore important to tailor the supported metal oxide cluster systems to achieve the desired reactivity and selectivity. Here, we present a scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) study of the monodispersed MoO_3 clusters deposited by the sublimation of MoO_3 powder on anatase TiO_2(101) surface at 300 K. After the deposition, the STM images of the lowest concentration of MoO_3 show that the clusters initially migrate over the surface and preferentially anchor at step edges before they start to aggregate on the terraces. Interestingly, the aggregates are mostly composed of three adjacent clusters, with a small concentration of monomers and dimers. Further exposures to MoO_3 increase the cluster coverage until a fully saturated over-layer is created with each clusters being are centered on top of the Ti sites. The adsorbed clusters appear as bright protrusions, with an apparent cluster height of approximately 1.5 Å and diameter of about 8.5 Å. Since the cyclic $(MoO_3)_3$ trimers are known to be a dominant gas phase species resulting from the sublimation of MoO_3 [1], we propose that each cluster on the surface is a trimer. Annealing to 550 K results in a better-order of the $(MoO_3)_3$ layer, but further annealing to 650 K leads to three-dimensional clusters. The XPS results indicate that the Mo($3d_{5/2}$) binding energy in as-deposited $(MoO_3)_3$ is characteristic of Mo^{6+}, and the oxidation state of Mo remains (+6) upon heating to 600 K. As such, this system may offers great promise as an ideal platform for reactivity studies on well-defined supported model transition-metal oxide catalysts.

[1] Zdenek Dohnálek et al. Royal Society of Chemistry 43, 7664−7680 (2014).

12:00pm **SS+AS+HC+TL-ThM-13 Ionic Conducting Nanostructures Tailored on Porous Mixed Conduction Composite Electrodes for Enhancement of Oxygen Reduction Reaction***,* ***Jong-Eun Hong****, D Joh, S Kim, H Ishfaq,* Korea Institute of Energy Research, Republic of Korea*; C Jung, J Park,* DGIST, Republic of Korea*; S Lee, H Kim, T Lim, S Park, R Song,* Korea Institute of Energy Research, Republic of Korea*; K Lee,* DGIST, Republic of Korea

With decrease in the operation temperature of solid oxide fuel cells, the oxygen reduction reaction (ORR) in the cathodes, which is sluggish, plays an important role in improving the electrochemical performance. Much effort has given to facilitate the ORR by the applications of cathode surface modification using active catalysts, nano-particle cathodes, and advanced cathode materials. In particular, the cathode surface modification with a reactive electro-catalyst has been appeared to increase the electrode reactivity and thus to decrease the polarization resistance to the oxygen reduction reaction. Infiltration of electro-catalysts has been widely utilized to tailor the cathode microstructures as it is a facile method. In this study, one-step infiltration using an in-situ sol–gel process was applied to modify porous mixed conducting composite cathodes, and the impact of surface microstructure tailoring on the electrochemical performances was investigated. The precursors of Sm- and Nd-doped ceria (SNDC), whose ionic conductivity is even higher than that of Gd-doped CeO_2 (GDC), were infiltrated into the cathode by using an ultrasonic spray nozzle to produce fine and uniform droplets. The infiltrated samples then experienced an in-situ heat-treatment after repeating the ultrasonic spraying and drying processes and were submitted for electrochemical measurements. The detailed results on the microstructure evolution and electrochemical properties of the specimens prepared using the ultrasonic spraying infiltration are presented, and the elucidation of the results are discussed.

2D Materials
Room A216 - Session 2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA
Surface Chemistry, Functionalization, Bio, Energy and Sensor Applications

Moderator: Mark Edmonds, Monash University, Australia

2:20pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-1 Molecular Layers on Nanoporous Gold Electrodes***, **Elizabeth Landis,*** College of the Holy Cross

Nanoporous gold presents a surface with high conductivity and surface area, which makes it an interesting platform for surface chemistry. However, the nanoporous gold surface lacks the functionality necessary for many applications including sensing. We have investigated self-assembled thiol-based monolayers and the electroreduction of diazonium-based salts to form aryl molecular layers on nanoporous gold. We use infrared spectroscopy and cyclic voltammetry to show that the molecular layer ordering and density depends on the functionalization method, and the underlying nanoporous surface impacts molecular ordering and electron transfer properties.

2:40pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-2 Thermotropic Liquid Crystal (5CB) on Two-dimensional Materials***, **Paul Brown,*** American Society for Engineering Education*; S Fischer, J Kołacz, C Spillmann, D Gunlycke,* U.S. Naval Research Laboratory

Current means of redirecting light often rely on either bulky mechanical gimbals or non-mechanical diffractive elements. The former often suffer from wear and are susceptible to failure, while the latter may have significant optical power confined within side lobes. One promising non-mechanical approach that can overcome present limitations in beam redirection incorporates liquid crystal (LC) for continuous, refractive steering. Nematogens, the molecules comprising the LC in a nematic phase, support inherent anisotropic optical and dielectric properties that result from local ordering of single molecules. Recent research suggests the possibility of including two-dimensional materials to act as both an alignment layer and electrode to LC. This offers the possibility of further reducing device dimensions and device response time. Yet little research has focused on the ground state properties of a nematogen interfacing with the two-dimensional substrate. In this talk, we present density functional theory results of the electronic properties of a well-known nematogen (5CB) interacting with graphene, boron nitride, and phosphorene. We also discuss the influence of an introduced single vacancy on the electronic properties of the composite system. We find that 5CB on phosphorene offers the strongest binding of the considered nanosheets. Moreover, we observe qualitatively different band alignments, and focus in particular on type I, which prohibits free carrier transfer between the substrate and nematic LC. Lastly, we discuss the impact of single vacancies on the performance of two-dimensional materials to operate as both an alignment layer and electrode for LC-based applications.

This work has been supported by the Office of Naval Research, directly and through the U.S. Naval Research Laboratory.

3:00pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-3 Is it Possible to Achieve Intra-molecular Resolution with Ambient AFM?***, **Vladimir Korolkov,*** Oxford Instruments-Asylum Research*; S Chulkov, M Watkins,* University of Lincoln, UK*; P Beton,* The University of Nottingham, UK

Although achieving molecular resolution is now almost a routine across various SPM imaging modes, resolving the actual molecular structure at the atomic level has only been accomplished with NC-AFM in UHV often at low temperatures and with a functionalized probe. Of course, the ultimate goal in SPM is to resolve the chemical structure of a molecule identifying each atom.

In this work we are presenting an approach to achieve intra-molecular resolution on adsorbed molecules in the ambient at room temperatures with a standard AFM cantilever with unmodified tip. We have discovered that using a combination of higher eigenmodes and low oscillation amplitudes (~3-5Å) of a standard Si-cantilever routinely provides ultra-high resolution on adsorbed molecules on surfaces[1,2] and bulk polymers[3].

With this approach we have been able to observe both intra-molecular features and inter-molecular contrast in thin films of coronene and melem molecules on the surface of hexagonal boron nitride (hBN). In case of coronene, all six benzene rings have been resolved as well as underlying atomic lattice of hBN. Unlike coronene, melem forms molecular assemblies with square symmetry stabilized with in-plane strong hydrogen bonds between amino groups. We have observed a strong inter-molecular contrast where the hydrogen bonds are expected to be. Similar to coronene, the observed intra-molecular contrast was associated with three triazine rings. We have used Probe particle model[4] to simulate our experimental AFM images and found very good agreement between them. In fact, PPM allowed us a correct interpretation of melem square phase assembly.

Both systems were studied at room and elevated temperatures where we observed phase transitions leading to thermodynamically stable systems. The experimental results are in excellent agreement with density functional theory calculations.

We believe the proposed approach, yet still in its infancy, could potentially provide a pathway to unambiguous identification of molecules on surfaces in the ambient on standard AFM systems.

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[1] Korolkov et al., Nat. Chem., 2017

[2] Korolkov et al., Nat. Comm., 2017

[3] Korolkov et al., Nat. Comm., 2019

[4] Hapala et al., Phys. Rev. B 90, 085421

3:20pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-4 Tailoring Surface Properties via Functionalized Hydrofluorinated Graphene Compounds***, **Jangyup Son,*** University of Illinois at Urbana-Champaign*; N Buzov,* University of California at Santa Barbara*; S Chen,* University of Illinois at Urbana-Champaign*; D Sung,* Sejong University, Republic of Korea*; H Ryu,* Seoul National University, Republic of Korea*; J Kwon,* Yonsei University, Republic of Korea*; S Kim, J Xu,* University of Illinois at Urbana-Champaign*; S Hong,* Sejong University, Republic of Korea*; W King,* University of Illinois at Urbana-Champaign*; G Lee,* Seoul National University, Republic of Korea*; A van der Zande,* University of Illinois at Urbana-Champaign

Mixing compounds or alloys is an important process to tailor or enhance the intrinsic properties of materials such as chemical reactivity, mechanical strength, and electronic structure. In nanosystems, such as two-dimensional (2D) materials like graphene, transition metal dichalcogenides (TMDCs), and hexagonal boron nitride (hBN), where there is no distinction between the surface and the bulk, mixing of elements is also an important tool for tailoring the interaction of the material with its environment. A successful strategy for manipulating the chemical structures of 2D materials is the chemical functionalization of graphene with single elements such as H, O, N, and F. Yet, an even wider parameter space is possible by combining these functionalization species to produce ternary functionalized graphene compounds.

Here we present a new strategy for producing functionalized graphene compounds through the systematic control of the ratio between adatoms. We demonstrate tailored hydrofluorinated graphene (HFG) compounds via the sequential exposure of graphene to low-energy hydrogen plasma and xenon difluoride (XeF_2) gas. We demonstrate reversible switching of the surface between completely hydrogenated graphene (HG) and fluorinated graphene (FG) as well as the intermediate ratio between two extremes. Moreover, we demonstrate pattern the surface functionalization on a single chip into chemically distinct materials (graphene, FG, HG, and HFG compounds).

Finally, with these patterned structures, we demonstrated tailoring of the surface and electronic properties of the 2D materials. First, the patterned structures enable direct comparisons of the relative surface properties such as wettability and surface friction. Additionally, the electrical properties of functionalized graphene compounds showed unusual recovery of electrical conductance during the partial transformation of FG to HFG, due to initial removal of existing F adatoms when exposed to hydrogen plasma. This study opens a new class of 2D compound materials and innovative chemical patterning that can lead to atomically thin 2D circuits consisting of chemically/electrically modulated regions.

4:00pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-6 Functionalization of MoS_2 with Halogens***, G Copetti,* IF-UFRGS, Brazil*; E Nunes,* IQ-UFRGS, Brazil*; G Soares,* IF-UFRGS, Brazil*; **Cláudio Radtke**,* IQ-UFRGS, Brazil

Transition metal dichalcogenides (TMDs) with lamellar structures similar to that of graphite have received significant attention because some of them are semiconductors with sizable bandgaps and are naturally abundant. This offers opportunities for fundamental and technological research in a variety of fields including catalysis, energy storage, sensing, and electronic devices. In order to TMDs fulfill their potential, a precise control i) of surface functionalization and ii) of the number of stacked TMD monolayers are mandatory. Surface functionalization was shown to play a key role in tuning photoluminescence properties of MoS_2, formation of controllable and low defect density dielectric/MoS_2 interfaces obtained by atomic layer deposition, and etching of MoS_2 layers. Halogenation is one of the most promising functionalization techniques of TMDs. MoS_2 etching with atomic layer control was already achieved by chlorine adsorption associated with Ar^+ sputtering. Moreover, doping techniques to tune the conductivity and photoemission properties of MoS_2 are essential. Previous works have already shown that incorporation of F-containing species in MoS_2 leads to doping, as well as other interesting properties such as tunable ferromagnetic ordering. In this work, we performed first principal calculations with the density functional theory (DFT) to gain insight into the effect of MoS_2 exposure to halogens. Results evidenced different reactivities while comparing F and Cl, as well as MoS_2 surfaces with variable amounts of defects. These results were explored experimentally. Bulk exfoliated MoS_2 as well as CVD-grown monolayer MoS_2 samples were used. Chlorination was achieved by irradiating the samples with UV light in Cl_2 flux. Prior to chlorination, sputtering of the MoS_2 with Ar ions is performed to induce S removal. X-ray Photoemission Spectroscopy measurements and Rutherford Backscattering Spectrometry showed that S vacancies play a fundamental role in the chlorination process, with vacancy concentration dictating the balance between etching of the MoS_2 layer and Cl incorporation. Fluorination was performed by exposing the samples to pulses of XeF_2. Different degrees of fluorination are achieved by varying exposure time. S is removed and F is incorporated without any loss of Mo. Chemical displacement on the Mo 3d and S 2p XPS peaks was observed after both halogenations processes. These results can clarify the mechanisms of Cl and F incorporation. Finally, the halogenation techniques proposed can be simple and useful methods to adapt the MoS---$_2$ properties for future applications.

4:20pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-7 Towards Higher Alcohol Synthesis from Syngas on 2D material-based catalysts: A First-Principles Study****, Tao Jiang,*** *D Le, T Rahman,* University of Central Florida

Synthesis of higher alcohol from syngas has been of great interest owing to the limited petroleum resources and environmental concerns. Rational designing of cheap and efficient catalyst material for such synthesis is in great demand because of diminishing supply of the current state-of-the-art catalysts. Two dimensional (2D) materials are emerging with far-reaching potential for technical and industrial applications thanks to their unique properties, recent developments and improvement of production technologies. In this talk, we will discuss our recent work, based on first principles calculations, towards the unitization of 2D materials as catalysts for higher alcohol synthesis. In particular, defect laden hexagonal boron nitride (*dh*-BN) with N vacancies is excellent catalyst for hydrogenation of CO_2 towards ethanol formation, in the reaction pathway of which thecrucial step for forming C_2 bond, i.e. reaction of adsorbed species CH_3* and CO* to form CH_3CO*, is exothermic with reasonably low activation barrier (0.68 eV). On the other hand, we also find single layer of MoS_2 functionalized with small Au nanoparticle to catalyze CO hydrogenation reaction towards ethanol formation. Among all the elementary reactions, the important steps are the reaction of an adsorbed CH_3* and a CO* molecule and the hydrogenation of acetyl to acetaldehyde (both are exothermic with activation barriers of 0.69 and 0.47 eV, respectively) to form C_2 species.[1] The results suggest that 2D materials are suitable candidates for higher alcohol synthesis. Full reaction pathways will be discussed together with results of Kinetic Monte Carlo simulations to shed light on the selectivity of the catalysts. Contact will be made with experimental data that validate our theoretical predictions.

[1] K. Almeida, K. Chagoya,A. Felix, T. Jiang et al, "Towards Higher Alcohol Formation using a single-layer MoS_2 activated Au on Silica: Methanol Carbonylation to Acetaldehyde", submitted

*Work supported in part by DOE Grant DE-FG02-07ER15842

4:40pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-8 Proton Conductivity Properties of Electrospun Chitosan Nanofibers***, **Woo-Kyung Lee**, J Pietron, D Kidwell, J Robinson, C McGann, S Mulvaney,* U.S. Naval Research Laboratory

A major challenge of the 21st century will be to establish meaningful two-way communication between biology and electronics. The study of protonics, devices that mimic electronics but pass protons instead of electrons, seeks to bridge this gap. Protonic conductive materials (PCMs) are essential elements of these devices and we have demonstrated significant improvement in conductivity for chitosan PCMs when deposited as electrospun nanofibers. The observed improvements stem from both enhanced molecular alignment and from chemical doping due to the electrospinning carrier fluid, trifluoroacetic acid (TFA). We deposited electrospun chitosan nanofibers over palladium protodes and then used the helium ion microscope to isolate single nanofibers for detailed study. We observed that single chitosan nanofibers are strongly doped by TFA with x-ray photoelectron spectroscopy demonstrating extensively protonated nitrogen functionality. With the isolated, single chitosan nanofibers we observed that water uptake, fiber/electrode contact area, and doping concentration are critical parameters of protonic device performance and lead to increased conductivity (*i.e.* low resistivity). The average resistivity of single chitosan nanofibers is 6.2×10^4 Ω·cm, approximately two orders of magnitude lower than the resistivity of cast chitosan PCMs (cast from acetic acid solutions not TFA).We have observed excellent agreement between theoretical models and experiment results that explore each of the contributions to the improved conductivity. In addition, the fabrication and measurement of ionic field-effect transistor of single chitosan fiber using conductive atomic force microscope will be discussed.

5:00pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-9 Sensor for Breath and Skin Diagnostics***, **Pelagia I Gouma**,* The Ohio State University

Resistive gas sensors have received a bad reputation of being largely non-selective.

Our work has produced a crystallo-chemical model for selective gas sensing by polymorphic

metal oxides. The reaction-based and ferro-electric poling sensing mechanisms are discussed

in detail. Novel processing methods to produce the respective nano sensors are presented along

with the device fabrication for the non-invasive diagnosis of gaseous biomarkers in human

and animal breath or skin. This sensor technology is expected to revolutionize medical diagnostics.

5:20pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-10 Symmetry Controlled Ddsorption of Diodobenzene on MoS_2***, **Zahra Hooshmand**,* University of Central Florida*; P Evans, P Dowben,* University of Nebraska - Lincoln*; T Rahman,* University of Central Florida

In a joint experimental and theoretical study, we have uncovered evidence of the importance of symmetry in the adsorption of the isomers of diiodobenzene on MoS_2(0001). The intensity ratio of iodine to molybdenum measured, as a function of exposure for different isomers of the diiodobenzene, show that while for ortho (1,2-) and para (1,4-) diiodobenzene the rate of adsorption at 100 K is very low, that for meta (1,3-) diiodobenzene is considerably more facile. We have applied dispersion corrected density functional theory-based calculations to understand the subtleties in the electronic structure and geometry of adsorption of these diiodobenzene isomers on MoS_2(0001). All three isomers are found to weakly chemisorb with the same binding strength as well as adopt similar configurations. The calculated electron affinity of the three molecules also do not show a specific trend that would verify experimental data. However, analysis of the frontier orbitals indicate that those of 1,3-diiodobenzene are strongly affected by interactions with MoS_2, while that of the other two isomers remain unchanged. Our results show that symmetry is the identifying factor in these adsorption characteristics. The results of frontier orbitals analysis confirm that for adsorption of (1,2-) and (1,4-) diiodobenzene a reduction in the symmetry of the adsorbent is needed. To further validate our conclusions, we compare the above results with that of the adsorption of the diiodobenzene isomers on defect-laden MoS_2(0001).

* Work support in part by DOE grant DE-FG02-07ER15842

5:40pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-11 Mechanistic Understanding of the CO Hydrogenation Reaction on Defect Engineered 2D-TaS_2 and 2D-MoS_2 Catalysts***, **Mihai Vaida**,* University of Central Florida

Due to global energy demands, investigation of catalytic reaction mechanisms on novel catalytic materials that can lead to efficient production of storable fuels from sustainable inputs is of central importance. In this contribution the adsorption of CO and H_2 molecules, as well as the CO hydrogenation reaction are investigated on defect engineered two dimensional (2D) TaS_2 and MoS_2. Crystalline 2D-TaS_2 and 2D-MoS_2 with surface area of 1 cm^2 are synthesized via a multistep process based physical vapor deposition on Cu(111). The surface composition, morphology, and electronic structure are investigated via Auger electron spectroscopy, low energy electron diffraction, scanning tunneling microscopy, scanning tunneling spectroscopy, and photoemission spectroscopy. The interaction of the molecules with the surface and the catalytic reaction mechanisms are investigated via temperature programmed desorption/reaction. No catalytic reactions have been observed on crystalline 2D materials. However, an enhanced catalytic activity is observed after the generation of sulfur vacancies via Ar sputtering. The CO hydrogenation on TaS_2 occurs on low coordinated Ta atoms through the formation of formyl radical (HCO) and formaldehyde (HCOH). On 2D-MoS_2, the CO hydrogenation also occurs on low coordinated Mo atoms. However, in this case the formyl radical splits to form methyldyne radical (CH), which subsequently react with other CH radical to produce acetylene (C_2H_2).

Applied Surface Science Division
Room A211 - Session AS-ThA
Role of Surfaces and Interfaces in Energy Material and Industrial Problems

Moderators: David M. Carr, Physical Electronics, Alan Spool, Western Digital Corporation

2:20pm **AS-ThA-1 Characterization of Glass and Durable Optical Surfaces and Their Modes of Failure***, **Albert Fahey**, D Baker, T Dimond,* Corning Inc. **INVITED**

Glass has become the all-important interface between human users and information and communications in our daily lives. People not only want to look at bright, high-definition information-displays but also want to interact with and touch the displays. This has placed new requirements on the performance and durability of the surfaces we interact with.

Just below the outer boundaries of glass, the composition makes a transition from the surface that we interact with, defining the spatial limits of the solid, to the "bulk"-material that exhibits most of the macroscopic properties we experience that allow us to use it as building materials to construct displays, hand-held devices, smart-watches, etc.

The composition of the near-surface region, from a few nanometers to several micrometers generally governs the appearance and durability of these surfaces. It also is a critical component in the adhesion of thin films deposited to improve scratch resistance, cleanability, and optical performance.

We will review some compositional profiles of glass, thin films and other materials to understand how some of these surfaces appear, compositionally, and how this can inform us of chemistries and mechanical properties. I will review Secondary Ion Mass Spectrometry (SIMS) depth-profile data and its combination with data acquired by other methods that give us a more complete understanding of the optical surfaces we interact with.

3:00pm **AS-ThA-3 Determination of Liquid Laundry Additives Across Fabric Surfaces***, **Michael Clark, Jr.**, A Peera, S Donovan, R Pulukkody,* The Dow Chemical Company

Products that offer sensorial benefits in addition to cleaning are increasingly popular among consumers in the fabric care market. Such sensorial attributes are typically related to touch and smell and help provide a more enjoyable experience to the consumer both during and after the laundering process. This presentation will focus on the XPS and SIMS characterization of fabrics before and after washing with different liquid laundry formulations to determine the amount and distribution of different components on the fabric's surface.

3:20pm **AS-ThA-4 Depth Profiling of Silicones with GCIB, Do They Behave like Organic or Inorganic Molecules?***, **Michaeleen Pacholski**, M Clark, Jr., P Vlasak, C McMillan,* The Dow Chemical Company

Surface analysts have a love-hate relationship with silicones. Silicones are widely used industrially for lowering surface energy, improving slip, coefficient of friction, mar and many other surface lubricity properties. Due to their low surface energies, and sometimes low viscosity or molecular weight, there is a tendency for them to spread over surfaces or be present as surface contaminants. In these cases a surface analyst may wish to remove them using a gas cluster ion beam source (GCIB). In other instances it may be desirable to understand the chemistry of a silicone coating as a function of depth. Unfortunately, GCIB profiling of silicones is not as straightforward as it is with other organic polymers. Examples of depth profiles under different GCIB conditions from some reference silicones and silicone-containing coatings will be discussed in this presentation.

4:00pm **AS-ThA-6 Active Control of Interfacial Chemistry for Thin Film Solar Cells***, **Alexandra Koziel**, K Montiel, L Wilson, J Carter, I Martin,* Case Western Reserve University

Global energy demand requires the development of efficient and reliable thin film photovoltaics with inexpensive processing. As the efficiency of hybrid perovskite solar cells has skyrocketed, practical constraints of the technology have put the scalability and durability into scientific focus. The development of inorganic interfacial layers, such as metal oxides, is a potential pathway to overcoming the stability and cost limitations associated with organic interlayers in perovskite solar cells. Thin films are sensitive to both the growth conditions, and the composition and morphology of the previously deposited layer. Interfacial engineering of metal oxides using molecular modifiers provides a powerful tool to tune interlayer properties, which can result in improved performance and stability.

This work details the effect of underlying layers on the growth of $CsGeI_3$, a novel all-inorganic perovskite absorber. The hole-transport layer (HTL) and the underlying substrate were systematically varied. Surface and bulk properties of the film stack were characterized at every growth step. The choice of HTL affects the absorber film morphology, and resulting device efficiency. Further, this approach reveals that the choice of substrate can affect the properties of layers through the entire device.

Two common HTLs, PEDOT:PSS and MoO_3, were deposited on substrates with differing surfaces. Glass, ITO (indium tin oxide, a common thin film solar cell transparent electrode), and Si substrates were selected to explore how a range of surface structures, from amorphous to polycrystalline to crystalline, affects the subsequent layers. The vapor-deposited MoO_3 was further modified with gas-phase treatments (UV-ozone and O_2 plasma exposure) and small molecules (silanization). Specifically, an IPTMS ((3-iodopropyl) trimethoxysilane) silanization procedure was developed to produce an iodine-terminated surface, for improved adhesion of the $CsGeI_3$ absorber layer. A suite of materials characterization methods were applied to the samples after each step of device fabrication to assess the evolution of morphology and composition. Bulk, surface, and interface characteristics were probed using UV-Vis absorption measurements, X-ray photoelectron spectroscopy, scanning electron microscopy, optical profilometry, and spectroscopic ellipsometry. Notably, the absorber film morphology and ultimately the stability of the film stack is sensitive to not only the HTL, but the nature of the material under the HTL (ITO vs. glass), demonstrating the influence of surface/interface properties across multiple layers in a device.

4:20pm **AS-ThA-7 Solar Energy From a Big-Picture Perspective to Nanoscale Insights via TOF-SIMS***, **Steven Harvey**,* National Renewable Energy Laboratory **INVITED**

We have used time-of-flight secondary-ion mass spectrometry (TOF-SIMS) at the National Renewable Energy Laboratory to investigate the performance and reliability of solar cell materials and devices, and we will present some recent work that highlights the versatility of TOF-SIMS. This work includes: 1) Multi-scale, multi-technique investigations of photovoltaic module failure including TOF-SIMS to enable insights into the root-cause mechanisms of module degradation at the nanoscale that are observed at the length scale of meters; 2) Investigations into the performance and stability of hybrid perovskite solar cell devices and 3) Using a combination of 1-D profiling and 3-D tomography to elucidate the fundamentals of incorporating dopants in CdTe solar cells.

5:00pm **AS-ThA-9 Investigation of Surface and Bulk Properties of Extended Surface PtNi and PtNiCo Catalysts***, **Sarah Zaccarine**,* Colorado School of Mines*; W McNeary,* CU Boulder*; S Shulda, S Mauger, K Hurst,* National Renewable Energy Laboratory*; A Weimer,* CU Boulder*; S Alia, B Pivovar,* National Renewable Energy Laboratory*; S Pylypenko,* Colorado School of Mines

Polymer electrolyte membrane fuel cells (PEMFCs) produce electricity with only heat and water as byproducts, but sluggish kinetics of the oxygen reduction reaction (ORR) at the cathode restrict widespread commercialization, motivating development of advanced catalysts such as the extended surface platinum nickel (PtNi) and platinum nickel cobalt (PtNiCo) nanowires investigated in this work.

These catalysts were synthesized using atomic layer deposition (ALD), a scalable route that allows controlled deposition of Pt on Ni or Co nanowires. Surface and bulk composition and structure of the PtNi and

PtNiCo nanowires was investigated as a function of synthesis conditions and a series of post-synthesis modifications. A variety of characterization techniques was used to gain a comprehensive understanding of structure-property-performance relationships. The catalyst was first studied using a combination of x-ray absorption near-edge structure (XANES) spectroscopy, extended x-ray absorption fine structure (EXAFS) spectroscopy, x-ray photoelectron spectroscopy (XPS), and scanning transmission electron microscopy (STEM) coupled with energy dispersive x-ray spectroscopy (EDS) hypermapping to obtain detailed complementary information about speciation and distribution of Pt and Ni, distinguishing differences between surface and bulk. Rotating disk electrode (RDE) testing was conducted to assess activity and stability of the catalysts. Differences between ALD-derived PtNi and PtNiCo samples will be discussed and compared to previously reported catalysts synthesized via spontaneous galvanic displacement (SGD). Catalysts were then integrated into membrane electrode assemblies (MEAs) and properties of the fabricated catalyst layers were investigated using STEM/EDS and transmission x-ray microscopy (TXM) to better understand the interfaces between catalyst and ionomer, with and without addition of carbon into the structure of the electrode. Our results demonstrate important advances in the performance of this class of materials achieved through optimization of surfaces and interfaces of the catalyst and catalyst layer.

5:20pm **AS-ThA-10 Interfaces in Electrodeposited Li-Ion Battery Electrodes**, ***Paul Braun,*** University of Illinois at Urbana-Champaign **INVITED**

Electrodeposition of electrode materials has the potential to enhance secondary battery performance and broaden the scope of available electrode form factors. For example, as we have shown, electrodeposited electrodes provide energy densities not achievable via conventional slurry-cast electrode processing methodologies. I will present our work on the electrodeposition of high performance silicon and tin-based Na and Li-ion anodes and $LiCoO_2$, $NaCoO_2$, $LiMn_2O_4$, and related Na and Li-ion cathodes. The electrolytically active materials were formed either as solid films, or where significant volume changes upon cycling are present, as a 3D mesostructured film. The capacities are near-theoretical, and in the case of the electroplated oxides, the crystallinities and electrochemical capacities are comparable to powders synthesized at much higher temperatures. What we have found, is that the interfaces, and interphases that may form during cycling, have significant impacts on the properties of the resulting electrodes. Understanding the properties of these interfaces/interphases is critical to understanding, and ultimately improving, overall cell performance.

Surface Science Division
Room A220-221 - Session SS+2D+AP+AS+OX+SE-ThA
Dynamics at Surfaces/Reactions and Imaging of Oxide Surfaces

Moderators: Irene Groot, Leiden University, The Netherlands, William E. Kaden, University of Central Florida

2:20pm **SS+2D+AP+AS+OX+SE-ThA-1 Adsorption, Reaction, and Diffusion of Energetic Reagents on Morphologically Diverse Thin Films**, ***Rebecca Thompson***[1][2]*, M Brann, S Sibener,* The University of Chicago

I present work from two studies illustrating the impact of condensed-phase film morphology on reaction kinetics and surface adsorption. To begin, I will discuss the **oxidative reactivity of condensed propene films**. This work is conducted in a state-of-the-art ultra-high vacuum chamber equipped for operation at cryogenic substrate temperatures. Time-resolved reflection absorption infrared spectroscopy (RAIRS) is used to track propene reactivity when films are exposed to a supersonic expansion of ground state oxygen atoms, $O(^3P)$. I demonstrate that propene reacts significantly on exposure, producing primarily propylene oxide and propanal. Oxide production is significant; partial oxidation products are rarely observed in gas phase studies and olefin oxides are incredibly important chemical intermediates in a variety of industrial processes. Regardless of initial film thickness, the reaction follows zero order kinetics, with a calculated activation energy of 0.5 kcal mol^{-1}. This low barrier closely matches that reported in gas phase studies, suggesting that the condensed-phase reaction is likely diffusion-limited. I also highlight that the propene deposition temperature has a substantial impact on reactivity. Films deposited below 50 K produce dramatically different RAIR spectra that correspond to a more amorphous film composition. These films are nearly unreactive with $O(^3P)$, indicating that oxygen diffusion is directly tied to the density and ordering in the more crystalline film.

This dependence on film structure is also observed in the second study, which explores **embedding in and adsorption on crystalline, non-porous amorphous, and porous-amorphous water ice films**. Using a combination of supersonic molecular beams, RAIRS and King and Wells mass spectrometry techniques, I demonstrate that direct embedding into the bulk is remarkably insensitive to film structure; the momentum barrier is identical between amorphous and porous-amorphous ice films. Below this barrier, however, sticking probabilities differ considerably between the different films, suggesting that the pore structure is more efficient at dissipating incident energy. These discoveries are critical for the accurate quantitative modeling of molecular uptake and reactivity on icy astrophysical bodies such as comets and planetismals. When taken together, these two studies provide fundamental mechanistic insight into the sticking, diffusion, and reactivity of small molecules on complex films, with a specific emphasis on the impact of film morphology and organization.

2:40pm **SS+2D+AP+AS+OX+SE-ThA-2 Oxidation of Semiconductors and Semimetals by Supersonic Beams of O_2 with Scanning Tunneling Microscopy Visualization**, ***Ross Edel***[3]*, T Grabnic, B Wiggins, S Sibener,* The University of Chicago

Our research examines the oxidation of semiconductor and semimetal surfaces using a novel, one-of-a-kind instrument that combines a supersonic molecular beam with an in-line scanning tunneling microscope (STM) in ultra-high vacuum. This new approach to surface reaction dynamics provides spatiotemporal information on surface oxidation over nanoscopic and mesoscopic length scales. We have uncovered the kinetic and morphological effects of oxidation conditions on three technologically relevant surfaces: Si(111)-7×7, highly oriented pyrolytic graphite (HOPG), and GaAs(110). A complete understanding of the oxidation mechanism of these surfaces is critical due to their technological applications and roles as model systems. Samples were exposed to O_2 with kinetic energies from 0.4-1.2 eV and impingement angles 0-45° from normal, with STM characterization between exposures. In some cases, we were able to monitor the evolution of specific features by revisiting the same nanoscopic locations. Our study of Si(111)-7×7 revealed two oxidation channels, leading to the formation of dark and bright reacted sites. The dark sites dominated the surface and exhibited almost no site selectivity while the bright sites preferred the corner sites of the 7×7 unit cell. Our observations suggest that two adsorption pathways, trapping-mediated and direct chemisorption, occur simultaneously. On HOPG, we found that different oxygen energies, incident angles, and surface temperatures produce morphologically distinct etching features: Anisotropic channels, circular pits, and hexagonal pits. Reaction probability increased with beam energy and demonstrated non-Arrhenius behavior with respect to surface temperature, peaking at around 1375 K. Finally, oxidation of GaAs(110) was found to proceed by two morphologically distinct, competing mechanisms: a homogeneous process leading to layer-by-layer oxide growth, and a heterogeneous process with oxide islands nucleating from surface defects. The rates of both mechanisms change with O_2 kinetic energy, with homogeneous oxidation dominating at lower energies (<0.7 eV) and heterogeneous oxidation with higher energies (≥1.0 eV). The results obtained in this work provide vital information about the morphological evolution and kinetics of semiconductor and semimetals, offering a comprehensive overview of the spatiotemporal correlations that govern oxidation dynamics on surfaces.

3:00pm **SS+2D+AP+AS+OX+SE-ThA-3 Studying Molecule-Surface Interactions using Rotational Orientation Control of Ground-State Molecular Beams**, ***Gil Alexandrowicz,*** Swansea University, UK **INVITED**

Performing quantum state selective experiments of molecule-surface collisions provides unique insight into the interaction potential. One particularly tricky molecular property to control and measure is the rotational projection states, i.e. the orientation of the rotational plane of the molecule. Previous data was mostly restricted to photo-excited/paramagnetic species. In this talk, I will describe the molecular beam apparatus which allows to control and measure the rotational orientation of ground state molecules [1], present new experimental results for H_2 colliding with ionic surfaces and discuss the future of this new

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

[2] **National Student Award Finalist**

[3] **National Student Award Finalist**

technique in terms of studying molecule-surface interaction-potentials and modifying the outcome of reactive molecule-surface collisions.

[1] Nature Communications, 8, 15357 (2017).

4:00pm **SS+2D+AP+AS+OX+SE-ThA-6 Diffusion of (100)-epitaxially Supported 3D fcc Nanoclusters: Complex Size-dependence on the Nanoscale***, King Chun Lai, J Evans,* Iowa State University

Diffusion of supported 3D nanoclusters (NCs) followed by coalescence leads to coarsening of ensembles of supported NCs via Smoluchowski Ripening (SR) which is a key pathway for degradation of supported metal catalysts. The dependence of the NC diffusion coefficient, D_N, on size N (in atoms) is the key factor controlling SR kinetics, and traditional treatments assumed simple monotonic decrease with increasing size. We analyze a stochastic model for diffusion of (100)-epitaxially supported fcc NCs mediated by diffusion of atoms around the surface of the NC. Multiple barriers for surface diffusion across and between facets, along step edges, etc. are chosen to accurately describe Ag [Lai and Evans, Phy. Rev. Materials 3 (2019) 026001]. KMC simulations reveal a complex oscillatory variation of D_N with N. Local minima D_N sometimes but not always correspond to $N = N_c$ where the equilibrium Winterbottom NC structure is a closed-shell. Local maximum generally correspond to $N = N_c + 3$. The oscillatory behavior is expected to disappear for larger N above $O(10^2)$. Behavior has similarities to but also basic differences from that for 2D supported NCs [Lai et al Phys. Rev. B 96 (2017) 235406]. Through detailed analysis of the energetics of the 3D NC diffusion pathway (which involves dissolving and reforming facets), we can elucidate the above behavior as well as observed trends in effective diffusion barrier.

4:20pm **SS+2D+AP+AS+OX+SE-ThA-7 Oxide Surface Formation on Rh Nanoparticle during O_2 Exposures Observed by Atom Probe Microscopy***, **Sten Lambeets**,* Pacific Northwest National Laboratory*; T Visart de Bocarmé,* Université Libre de Bruxelles, Belgium*; N Kruse,* Washington State University*; D Perea,* Pacific Northwest National Laboratory

Metallic surfaces may undergo a series of surface and subsurface structural and chemical transformations while exposed to reactive gases that inevitably change the surface properties. Understanding such dynamics from a fundamental science point of view is an important requirement to build rational links between chemical/structural surface properties and design new catalysts with desired performance or new materials with enhanced resistance to corrosion. The research presented here addresses the early oxide formation dynamics on a rhodium (Rh) single nanoparticle during O_2 exposures and reveals the inter-facet cooperation between Rh{012} and Rh{113} facets, as well as the important role that the subsurface plays.

Field Ion and Field Emission Microscopies (FIM and FEM) enable correlative atomic to nanoscale imaging of the surface of a very sharp Rh needle, the apex size and shape of which models that of a Rh nanoparticle. FIM is used to map, with atomic lateral resolution, the Rh surface revealing a complex network of crystallographic facets, while FEM is used to observe and record O_2 dissociative adsorption and subsequent reaction with H_2 over this same surface of Rh in real-time with nano-scale lateral resolution. Since FEM imaging relies on local work function variations, it notably can be used to follow the fate of adsorbed oxygen atoms (O(ads)) on the Rh surface. As a result, we directly observe that the O_2 dissociative adsorption is mainly active on the Rh{012} regions. The application of Atom Probe Tomography (APT) provided a means to map the fate of the absorbed oxygen leading to bulk oxide formation through Rh{113} facets. Thus the correlative combination of FIM, FEM, and APT provides unique insight into the mechanism of bulk oxide formation starting from the dissociative oxygen absorption occurring at {012} facets and subsurface penetration of the adsorbed oxygen occurring through {113} facets. leading to a preferential accumulation of the oxygen within the bulk along the [111] direction. This work offers a unique methodology to explore the interactions between the different crystal facets of a complex surface, to explore the complex dynamics linking the surface and the bulk, and finally, offers exciting perspectives leading to a better understanding of heterogeneous catalysis and corrosion dynamics.

4:40pm **SS+2D+AP+AS+OX+SE-ThA-8 Noncontact AFM on Oxide Surfaces: Challenges and Opportunities***, **Martin Setvin**,* TU Wien, Austria **INVITED**

Recent development of the noncontact atomic force microscopy (nc-AFM) has opened new possibilities in different fields – imaging of organic molecules [1], controlling the charge state of adsorbed species [2], or enhanced chemical resolution of surface atoms [3]. I will focus on the emerging possibilities and opportunities in the field of oxide surfaces and their surface chemistry.

The limits of atomic resolution will be illustrated on clean and water-exposed binary oxides like TiO_2, In_2O_3 or iron oxides. The enhanced chemical resolution of nc-AFM offers a unique opportunity for approaching complex materials with ternary chemical composition. This will be demonstrated on bulk-terminated perovskites $SrTiO_3$ and $KTaO_3$. A dedicated cleaving procedure [4,5] allows preparing flat regions terminated by domains of SrO/TiO_2 (or KO/TaO_2) with a well-defined atomic structure. The surface stability, point defects, electronic structure, and chemical properties of such surfaces will be discussed and linked to the incipient-ferroelectric character of these materials.

[1] Gross, L.; Mohn, F.; Moll, N.; Liljeroth, P.; Meyer, G., *Science* 2009, *325*, 1110

[2] Gross, L.; Mohn, F.; Liljeroth, P.; Repp, J.; Giessibl, F. J.; Meyer, G., *Science* **2009,***324*, 1428

[3] Sugimoto, Y.; Pou, P.; Abe, M.; Jelinek, P.; Perez, R.; Morita, S.; Custance, O., *Nature* **2007,***446*, 64

[4] I. Sokolovic, M. Schmid, U. Diebold, M. Setvin, *Phys. Rev. Materials* 3, 034407 (2019)

[5] M. Setvin, M. Reticcioli, F. Poelzleitner, J. Hulva, M. Schmid, L. A. Boatner, C. Franchini, U. Diebold, *Science* 359, 572-575 (2018)

5:20pm **SS+2D+AP+AS+OX+SE-ThA-10 Edge-Enhanced Oxygen Evolution Reactivity at Au-Supported, Ultrathin Fe2O3 Electrocatalysts***, **Xingyi Deng**, D Kauffman, D Sorescu,* National Energy Technology Laboratory

Transition metal oxides have been emerging as promising candidates to replace the state-of-the-art IrO_2 electrocatalysts for oxygen evolution reaction (OER) in alkaline electrolyte, but their key structure-property relationships are often shadowed by heterogeneities in the typical catalyst samples. To circumvent this challenge, we have combined ultrahigh vacuum surface science techniques, electrochemical measurements, and density functional theory (DFT) to study the structure-dependent activity of well-defined OER electrocatalysts. We present direct evidence that the population of hydroxylated Fe edge-site atoms correlates with the OER activity of ultrathin Fe_2O_3 nanostructures (~0.5 nm apparent height) grown on Au(111) substrates, and the Fe_2O_3/Au catalysts with a high density of edge sites can outperform an ultrathin IrO_x/Au OER catalyst at moderate overpotentials. DFT calculations support the experimental results, showing more favorable OER at the edge sites along the Fe_2O_3/Au interface with lower predicted overpotentials resulted from beneficial modification of intermediate binding. Our study demonstrates how the combination of surface science, electrochemistry, and computational modeling can be used to identify key structure-property relationships in a well-defined electrocatalytic system .

5:40pm **SS+2D+AP+AS+OX+SE-ThA-11 Adsorption and Reaction of Methanol on the Magnetite Fe_3O_4(001) Surface***, **Matthew Marcinkowski**,* Pacific Northwest National Laboratory*; K Adamsen,* Aarhus University, Denmark*; N Doudin, Y Yang Wang, S Smith, B Kay, Z Dohnalek,* Pacific Northwest National Laboratory

Methanol's interaction with iron oxide surfaces is of interest due to its potential as a hydrogen storage molecule, and from a fundamental perspective as a chemical probe for the reactivity of an oxide surface. We present here a study examining the adsorption and reaction of methanol on magnetite Fe_3O_4(001) at cryogenic temperatures using a combination of temperature programmed desorption (TPD), simulations, x-ray photoelectron spectroscopy (XPS), and scanning tunneling microscopy (STM). Methanol's desorption profile from Fe_3O_4(001) is complicated, exhibiting peaks at 145, 175, 238, and 273 K corresponding to the desorption of intact methanol, as well as peaks at 350 and 516 K due to the reaction of methoxy intermediates. The saturation of a monolayer of methanol corresponds to 4 molecules/ unit cell, equivalent to the number of surface octahedral iron atoms. We probe the kinetics and thermodynamics of the desorption of molecular methanol using inversion analysis. Deconvolution of the complex desorption profile into individual peaks allows for calculation of both the desorption barrier and pre-factor of each feature. Low temperature scanning tunneling microscopy is used to observe the structure corresponding to each of the molecular desorption features. 20% of the adsorbed methanol reacts to form a methxoy intermediate by 180 K, which remains on the surface above room temperature after intact methanol has desorbed. This methoxy reacts via one of two channels, a recombination reaction with surface hydroxyls to form additional methanol at 350 K, and a disproportionation reaction to form methanol and formaldehyde at 516 K. Only 20% of the methoxy species undergo the disproportionation reaction, with most of them reacting via the 350 K pathway. Our study provides a detailed view of the adsorption and reaction of methanol and its surface intermediate methoxy on $Fe_3O_4(001)$.

Thin Films Division
Room A124-125 - Session TF+AS+EL+PS+RA-ThA
Characterization of Thin Film Processes and Properties

Moderators: Richard Vanfleet, Brigham Young University, Virginia Wheeler, U.S. Naval Research Laboratory

2:20pm **TF+AS+EL+PS+RA-ThA-1 Phase Separation in III-V Semiconductor Thin Films***, **Mark Twigg**, N Mahadik, N Kotulak, S Tomasulo, M Yakes,* U.S. Naval Research Laboratory **INVITED**

Phase separation in III-V semiconductor alloys remains a problem that limits the performance of electronic materials. As the first stage in a comprehensive program addressing this issue, we have begun investigating an alloy system in which only the group III elements differ: InGaAs. Lattice-matched InGaAs alloy films were deposited at three temperatures (400, 450, and 500C) by molecular beam epitaxy on a (001) InP substrate.

According to kinetic instability theory, the critical temperature for spinodal phase separation in InGaAs is 814C, a temperature well above the growth temperatures used in this study [1,2]. Dark-field (DF) cross-sectional transmission electron microscopy (XTEM), using the composition sensitive g=002 reflection, was used to determine the amplitude of composition modulations averaged over the thickness of the XTEM sample. The amplitude of composition modulation was found to decrease with increasing growth temperature, yielding values of 0.6, 0.4, and 0.3 atomic percent for the growth temperatures 400, 450, and 500C, respectively, a trend in accord with kinetic instability theory. X-ray reflectivity and 2-dimensional small angle x-ray measurements also indicate that the 400C growth shows significantly greater phase separation than the 450 and 500C growths. Atom probe tomography indicates that the amplitude of composition modulation for the 400C growth is approximately 1 atomic percent, a value that compares favorably with the 0.6 atomic percent measured by DF XTEM.

The range of wavelengths for lateral composition modulation is found to extend from approximately 3 to 30 nm. According to the literature, such wavelengths have been found to depend on growth temperature for a number of III-V semiconductor alloys, in agreement with predictions based on surface diffusion. Measurements of the composition modulation wavelength as a function of temperature have been performed by analyzing DF XTEM images recorded using the g=220 diffraction vector, from XTEM samples with the glue line along the rapidly-diffusing [110] direction. Fast Fourier Transform (FFT) power spectra recorded from each image allowed the dominant composition modulation wavelengths to be determined. Analyzing these wavelengths as a function of temperature yields the same activation energy (0.55 eV) as that found in surface diffusion measurements for In adatoms on the (001) InGaAs surface [3]; thereby confirming the role of surface diffusion in phase separation driven composition modulations.

[1] F. Glas, Phys. Rev.B, 62, 7393 (2000).

[2] I. P. Ipatova, V. G. Malyshkin, and V. A. Shchukin, J. Appl. Phys. 7198 (1993).

[3] Stevens et al., J. Appl. Phys. 121, 195302 (2017).

3:00pm **TF+AS+EL+PS+RA-ThA-3 In-Situ Spectroscopic Monitoring of Methylamine-Induced Hybrid Perovskite Phase Transitions***, **Jonathan Meyers**[1], L Serafin, J Cahoon,* University of North Carolina at Chapel Hill

Lead halide perovskites have shown remarkable promise for use in thin film optoelectronic devices such as photodetectors, light-emitting diodes, and solar cells. Methods for casting thin films of perovskite have been extensively studied, and great improvements have been made in an effort to improve device efficiency and stability. A few reports have suggested some benefits to processing or post-processing techniques in a methylamine (MA) atmosphere, including healing grain boundary defects to create pinhole free films with grains on the order of tens of microns and improving crystallinity. The process can be observed spectroscopically as the MA induces a reversible phase change which bleaches the dark perovskite film. In this work, we perform the MA-treatment in a vacuum reactor while monitoring in-situ the UV-visible spectral response correlated with temperature and MA partial pressure. Clear evidence is found for the existence of a solid intermediate phase in transitioning from $MAPbI_3(s)$ to $MAPbI_3{*}xMA(l)$ and back again. We construct a phase diagram and demonstrate that the critical partial pressure of the phase transition changes from 10 to 500 torr between 25 and 120 °C. By tuning the kinetics of film crystallization, compact films with domains up to 80 µm can be produced.

3:20pm **TF+AS+EL+PS+RA-ThA-4 Angle-Resolved HAXPES Analysis of Al_xO_y and Cu_xO_y Layers formed by Metal Salt Diffusion into a poly 2-vinylpyridine (P2vP) Polymer Layer***, **Pierre Mani**,* Universidad Autonoma de Ciudad Juarez, México*; M Snelgrove,* Dublin City University, Ireland*; P Rueff,* Synchrotron SOLEIL, France*; R Lundy,* Trinity College Dublin, Ireland*; J Bogan, R O´Connor,* Dublin City University, Ireland*; J Enríquez,* Universidad Autonoma de Ciudad Juarez, México*; M Morris,* Trinity College Dublin, Ireland*; G Hughes,* Dublin City University, Ireland

This work is motivated by the desire to develop a semiconductor device patterning technology based on precursor infiltration into block copolymer materials. Developing an understanding of the preferential infiltration of metal precursors into one of the polymer blocks is of critical importance to advance this patterning approach. In this study, metal salts were used as a means to diffuse metal ions into poly 2-vinylpyridine (P2VP) polymer brush layers (~4 nm), which had been deposited by spin coating onto silicon substrates. Thin P2VP films infused with aluminum nitrate and copper nitrate by a wet chemical process were analyzed with angle resolved hard x-ray photoelectron spectroscopy (AR HAXPES). This photoemission based technique gives a lot information about a variety of core levels.[1] The large sampling depth of HAXPES measurements (20-30nm) enabled details of the chemical composition of the thin film to be characterized and subsequent angle-resolved HAXPES measurements offered a robust analysis of the interfaces and discrete layers that are present in the films. These measurements displayed evidence of bonding interactions between the elements in the polymer film and the infiltrated salts, which assists in developing an understanding of the infiltration process which needs to be optimized for device fabrication applications.[2]

[1] P. G. Mani-Gonzalez, M. O. Vazquez-Lepe, F. Espinosa-Magaña, and A. Herrera-Gomez J. Vac. Sci. Technol., A 31, 010601 (2013).

[2] C. Cummins and M. A. Morris. Using block copolymers as infiltration sites for development of future nanoelectronic devices: Achievements, barriers, and opportunities. Microelectron Eng., 195:74–85, 2018.

4:00pm **TF+AS+EL+PS+RA-ThA-6 Obtaining Smooth Surfaces and Measuring Surface Roughness***, **Steven M. George**,* University of Colorado at Boulder **INVITED**

Smooth surfaces are important in many areas including friction, adhesion, optics and film growth. Smooth surfaces can be obtained from rough surfaces using chemical mechanical polishing (CMP). Rough surfaces can also be smoothed using atomic layer deposition (ALD) if the conformal ALD film thickness is comparable with the lateral length scale of the roughness. In addition, rough surfaces can be smoothed using isotropic thermal atomic layer etching (ALE) if the ALE etch depth is comparable with the width of the surface asperities. Quantifying the degree of surface roughness after CMP, ALD or ALE is challenging. Surface roughness can be obtained using atomic force microscope (AFM) or x-ray reflectivity (XRR) measurements. However, the AFM and XRR techniques do not always agree. Some of the inconsistencies are attributed to the different lateral length scales for the AFM and XRR measurements. Using both AFM and XRR to characterize surface roughness is recommended for reliable measurements. In addition, XRR measurements for surface roughness should include both specular and diffuse off-specular scattering.

4:40pm **TF+AS+EL+PS+RA-ThA-8 Characterizing Ultra-thin Layer Growth and Area Selective Deposition using High Resolution Low Energy Ion Scattering (LEIS)***, **Thomas Grehl**,* IONTOF GmbH, Germany*; P Brüner,* ION-TOF GmbH, Germany*; V Pesce, B Pelissier, R Gassilloud, C Vallée,* Laboratoire des Technologies de la Microélectronique (LTM), France

When depositing ultra thin films of only very few nm of thickness, the characterization of the early stages of film growth is crucial for the quality of the film. For example, the initial thickness distribution before layer closure, created by the nucleation mechanism, will often remain after the film is complete. To analyze these early stages of growth requires very surface sensitive analytical techniques with good detection limits.

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[1] **National Student Award Finalist**

Specifically for area selective deposition, the demand for characterization increases even further. The deposition processes get more complex, involving atomic layer or plasma etching to remove nucleation on blocked areas. This also requires means of characterization, determining the effects of etching steps on the film being created, possible contamination and the level of success of the blocking.

One technique specifically suited for this application is Low Energy Ion Scattering (LEIS). By scattering noble gas ions from the surface of the sample, the mass of the atoms in the outer atomic layer is determined non-destructively. Due to specific charge exchange processes, the peaks in the scattering spectrum correspond only to the outer atomic layer, making LEIS the most surface sensitive technique to determine the elemental composition of a surface.

In addition, information from deeper layers is available in two ways: First of all, features in the spectrum contain information about the first few nm of the sample – especially for heavier elements, the in-depth distribution can be determined non-destructively. For more complex systems or light elements, sputter depth profiling can be applied as well.

In this presentation, we will illustrate the main features of LEIS on ALD films. The main part will be on an area selective deposition (ASD) process for Ta_2O_5 films on TiN or Si. Here, plasma-enhanced ALD (PE-ALD) and various plasma or ALE like etching processes, all using fluorine-containing compounds, are used to develop a super-cycle scheme for ASD. We show the effect of the different etching methods and use sputter depth profiling to determine the distribution of F – a light element not accessible to non-destructive depth profiling in LEIS. An important result is the distribution of F close to the surface, in the bulk of the film, or at the interface.

Besides this, some further sample systems will be used to highlight the use of LEIS for ultra-thin film characterization.

5:00pm **TF+AS+EL+PS+RA-ThA-9 Real-Time Monitoring of Aluminum Oxidation Through Wide Band Gap MgF_2 Layers for Protection of Space Mirrors**, *B Johnson, T Avval, G Hodges, K Membreno, D Allred,* ***Matthew Linford,*** Brigham Young University

Because of its extraordinary and broad reflectivity, aluminum is the only logical candidate for advanced space mirrors that operate deep into the UV. However, aluminum oxidizes rapidly in the air, and even a small amount of oxide (as little as a nanometer) can have a noticeable, detrimental impact on its reflectivity at short wavelengths. Thin films of wide band gap materials like MgF_2 have previously been used to protect aluminum surfaces. Here we report the first real-time, spectroscopic ellipsometry (SE) study of aluminum oxidation as a function of MgF_2 over layer thickness, which ranged from 0 – 6 nm. SE data analysis was performed vis-à-vis a multilayer optical model that included a thick silicon nitride layer. The optical constants for evaporated aluminum were initially determined using a multi-sample analysis (MSA) of SE data from MgF_2 protected and bare Al surfaces. Two models were then considered for analyzing the real-time data obtained from Al/MgF_2 stacks. The first used the optical constants of aluminum obtained in the MSA with two adjustable parameters: the thicknesses of the aluminum and aluminum oxide layers. The thicknesses obtained from this model showed the expected trends (increasing Al_2O_3 layer thickness and decreasing Al layer thickness with time), but some of the Al_2O_3 thicknesses were unphysical (negative). Because the optical constants of very thin metals films depend strongly on their structures and deposition conditions, a second, more advanced model was employed that fit the optical constants for Al, and also the Al and Al_2O_3 thicknesses, for each data set. In particular, the Al and Al_2O_3 thicknesses and optical constants of Al were determined in an MSA for each of 50 evenly spaced analyses in each four-hour dynamic run performed. The resulting optical constants for Al were then fixed for that sample and the thicknesses of the Al and Al_2O_3 layers were determined. While the first and second models yielded similar Al and Al_2O_3 thickness vs. time trends, the film thicknesses obtained in this manner were more physically reasonable. Thicker MgF_2 layers slow the oxidation rate of aluminum. The results from this work should prove useful in protecting space mirrors prior to launch. Detailed surface/material analysis by X-ray photoelectron spectroscopy will also be shown, as well as more advanced SE modeling.

5:20pm **TF+AS+EL+PS+RA-ThA-10 Visualization of Ultrafast Charge Motion in Thin Films via THz Emission Spectroscopy**, ***Aaron Lindenberg,*** Stanford University **INVITED**

We describe a method for probing ultrafast time-dependent currents in thin films and heterostructures by recording the associated emitted electromagnetic fields. This detection scheme offers direct sensitivity to the flow of charges at the atomic-scale and enables a real-time probe for investigating ultrafast charge transfer processes at molecular interfaces. Applied to transition metal dichalcogenide heterostructures having a staggered (Type-II) band alignment, we observe a burst of electromagnetic radiation at terahertz frequencies following above gap excitation. The emitted electric field transients encode information about the charge transfer within the heterostructure. The polarity of the emitted field reflects the direction of the charge transfer and the polarity is reversed as the order of the bilayer within the heterostructure is altered. We find that the charge transfer proceeds at an ultrafast rate (~100 fs) indicating a remarkable efficiency for the charge separation across these atomic-scale bilayers.

We will also describe initial experiments and coupled theoretical efforts probing charge separation and ultrafast photovoltaic responses in multiferroic BFO periodic domain structures. We show that charge separation occurs dominantly at the domain walls and provide a quantitative estimate of the efficiency of this process.

Applied Surface Science Division
Room Union Station AB - Session AS-ThP
Applied Surface Science Poster Session

AS-ThP-1 Hydrogen Generation Eases Safety and Infrastructure Requirements for Efficient and Productive Vacuum Deposition Processes*, David Wolff,* Nel Hydrogen

Hydrogen is frequently employed as a backfill gas during various vacuum coating processes involving metals. Hydrogen plays several roles and provides multiple benefits:

- As a carrier gas and diluent for active gases used to modify substrate surfaces

- As a cleaning and protective agent to clean deposition surfaces and prevent oxidation at high temperatures

- High purity hydrogen is relatively inexpensive, safe and effective in this application when used properly

The major challenge with hydrogen is the storage of hydrogen often required to have a source of pure hydrogen gas. Hydrogen gas for small and medium scale applications is generally delivered from far-away generating facilities and stored at the customer's site in the form of a compressed gas. Storage of hydrogen is closely controlled by national and international code guidelines and local Authorities Having Jurisdiction.

Proton Exchange Membrane (PEM fuel cell technology) hydrogen generation makes it possible to generate hydrogen at production rates and purity levels suitable for scientific and production applications. Most importantly, PEM hydrogen generation produces pure, pressurized, dry hydrogen in a load-following fashion without the need for hydrogen storage.

Poster will outline the code and cost advantages that PEM hydrogen generation can provide for scientific and production hydrogen use in vacuum applications.

AS-ThP-2 Progress in Understanding SIMS Spectra from Silicones*, **Paul Vlasak**, M 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.

Over the years we have observed variation in the fragmentation patterns and relative intensities of characteristic ions in the SIMS spectra from assorted PDMS-containing materials, however, the structural details that may influence the observed spectra remain poorly understood. In the past, we confirmed that endgroup type and molecular weight of PDMS fluids have a systematic influence on negative ion spectra. In addition, we determined that substrate type and thickness of the PDMS layer also greatly influence the spectra obtained, allowing us to hypothesize that the differing energy distributions and collisional cascades within the films and substrates strongly influence ion yields [1].

Using well-characterized PDMS reference materials spin-coated on a variety of substrates, the effects of cluster ion versus monoatomic ion sputtering will be presented as an extension of our past work. In addition, we previously demonstrated that spectra from a particular PDMS fluid became independent of substrate type as film thickness increased beyond the penetration depth of the primary ions, while current work further explores the sub-monolayer regime. Lastly, using thin films of various PDMS mixtures, investigation of potential layering of PDMS as a function of molecular weight or endgroup type will be presented.

[1] Vlasak, P.R.; Pacholski, M.L. (2018, October) *Differentiating Silicones Using SIMS*; presented at AVS 65th International Symposium & Exhibition, Long Beach, CA.

AS-ThP-3 Silicon Wet Etching Using NH4OH Solution For Texturing of Silicon Micro-Channels*, **José Alexandre Diniz**, A Silva,* UNICAMP, Brazil

This work presents the surface texturing of the horizontal wall of silicon micro-channels (SiMCs) using the NH4OH solution. The micro-channels are obtained on the backside of Si substrates, where the solar cells are fabricated. The micro-channels are used as heat sinks through which fluid will flow, such as water or alcohol. The texturing results in the micro-channels with roughness (in micro-pyramid shape) on horizontal surface. The roughness assists in the dilution of bubbles that can occur inside the fluid, because if the bubble excess occurs into the fluid, this can difficult the transport into the SiMC. The texturing is based on the formation of micro-pyramids with the use of NH4OH (ammonium hydroxide) alkaline solution etching, which is anisotropic. Our NH4OH solution etching can control the size of micro-pyramids on the surface into the SiMC This occurs because the etch rates are different for three [100], [110] and [111] Si crystal planes. The Si etching is due to the presence of the OH- (hydroxyl) in the NH4OH solution that reacts with Si. The micro-pyramids occurs because the (100) mono-crystalline substrates have a lower Si surface density of the plane than the (110) plane. The difference in density causes the etch rate for (100) plane to be greater than (110), which in turn, is greater than for (111). Thus, since it is a surface with lower density is easier penetration of the solution, which facilitates the Si reaction with hydroxyl (OH -). Anisotropic etching is obtained by alkaline solution of monocrystalline Si substrate, with (100) surface orientation. Exposure of [111] crystal plans occurred, forming the micro-pyramids. The obtained values of micro-pyramid height of 770 nm and 920 nm, when compared with a desired micro-channel depth of 200 µm, represent a ratio (between roughness and channel depth) lower than 5%. This ratio is considered suitable to reduce a significant impact on micro-channel performances.

AS-ThP-4 Ionic Liquids: Advanced Oil Additives for Lubricating Case-Hardened Titanium Alloys (OD-Ti64)*, **Harry Meyer III**, H Duan, W Li, C Kumara, Y Jin, H Luo, J Qu,* Oak Ridge National Laboratory

Titanium alloys possess many excellent characteristics (corrosion resistance, high fatigue strength and high strength-to-weight ratio) that has led to many important applications in several field (aerospace, bioengineering, automotive, etc.). However, these same alloys have only limited use as tribological materials due to abrasion and adhesion resistance. We previously investigated the use of oxygen-diffused Ti64 (OD-Ti64) and found that, in dry sliding conditions, the oxygen diffusion treatment improved the wear resistance compared to untreated Ti64. OD-Ti64 performed better than untreated Ti64, with respect to wear resistance when a lubricant containing ZDDP because of the formation of a ZDDP-based protective triobfilm.

This study extends these previous investigations by evaluating the use of ionic liquids (ILs) as oil additives to lubricate oxygen-diffusion (OD) case-hardened titanium for improved friction and wear behavior. A base oil for boundary lubrication of an OD-treated Ti-6Al-4V sliding against a steel ball was tested using four oil-soluble ILs used as additives. This poster will present data that will show (1) the ILs improved the friction behavior to various extents; (2) two phosphate ILs clearly outperformed conventional ZDDP; (3) ILs exhibited excellent wear protection suggesting good material-chemical compatibility; and (4) the carboxylate IL protected the OD-Ti surface from any measurable wear. The morphology and chemical composition of the worn surfaces and tribofilms were examined using a combination SEM, TEM, EDS, and XPS.

Research sponsored by Vehicle Technologies Office, Office of Energy Efficiency and Renewable Energy, U.S. Department of Energy (DOE). Electron microscopy characterization was in part performed at ORNL's Center for Nanophase Materials Sciences, sponsored by the Scientific User Facilities Division, Office of DOE-BES. The support by the National Natural Science Foundation of China (No. 51575402) and Chinese Academy of Sciences (CAS) during the visits of H. Duan and W. Li to ORNL, respectively, are also appreciated. This abstract has been authored by UT-Battelle, LLC under Contract No. DEAC05-00OR22725 with the U.S. Department of Energy.

AS-ThP-5 Controlling Surfaced-catalyzed Coupling of Aryl Halides for Preparation of Two-dimensional Covalent Networks*, **Margaret Wolf**, C Gerber, R Quardokus,* University of Connecticut

Formation and design of two-dimensional carbon-based materials can be controlled through surface-catalyzed reactions of small molecules. We use low-temperature scanning tunneling microscopy (LT-UHV STM) to monitor and characterize the surface-catalyzed reaction of dibromobenzene and dibromobithiophene. The Ullmann-like and Yamamoto-like coupling on

Au(111) lifts the gold herringbone reconstruction and the gold atoms and coupled adsorbate are mobile at 4 K. Annealing results in two-dimensional covalent networks and restores the gold herringbone reconstruction.

AS-ThP-6 Characterization of Mineral Associated Organic Matter in Alkaline Soil*, **Mark Engelhard**, R Kukkadapu, T Varga, R Boiteau, L Kovarik, J Cliff, M Wirth, A Dohnalkova, C Smallwood, D Perea, J Moran, K Hofmockel,* Pacific Northwest National Laboratory

Warden Soil (alkaline, fine sandy loam) from Prosser, WA was characterized by a suite of spectroscopic and microscopic techniques to gain insights into the nature of mineral-associated soil organic matter (SOM) and its stability under environmental perturbations (e.g., after spiking the soil with siderophores, fluctuating redox conditions, etc.). This approach was undertaken since: a) SOM associated with minerals has been recognized to be relatively stable with respect to biological degradation compared with particulate organic matter (POM), and b) the stability of mineral-OM moieties is primarily a function of interaction between the mineral and OM type, and their physical accessibilities by organisms, oxidants, etc.

Coupled Mössbauer spectroscopy and XRD measurements revealed that ~60-65% of total Fe (5.5 wt.%) in the soil was present in feldspars. The balance of the Fe was primarily partitioned as magnetite, ilmenite, and a suite of nano-Fe(III)-oxides. Various forms of Ca were evident in TEM as: a) "Ca-OM polymers", b) $CaCO_3$ coated with Ca-OM (consistent with XPS results), and c) Ca feldspar. OM-coated magnetite particles were also evident in TEM results. XPS measurements also demonstrated various types of surface organic C (20-25× that of bulk): a) aliphatic and aromatic C-(C-H), such as C-C, C=C, C-H, b) C-(O,N) bonds as in carbohydrates and amines, c) C displaying bonds to oxygen as in aldehydes, ketones, and amides (C=O, O-C-O, O=C-N), and iv) carboxylic C (O-C=O. NanoSIMS results of ^{13}C- and ^{15}N-labeled siderophore-spiked soils showed that Ca-OM phases rather than Fe-OM phases were preferential hosts for siderophores implying weaker but quickly forming interactions were preferentially established and stable enough to exist in calcareous environments. This provides a potential explanation of the lack of pyoverdines/catechols (siderophores) observed in grassland soils, and more broadly demonstrates the importance of adsorption kinetics rather than thermodynamic equilibrium on the fate and preservation of SOM.

AS-ThP-7 Atomic Structure Simulation of Nitrogen Supersaturated Austenitic Stainless Steel*, **Honglong Che**, M Lei,* Dalian University of Technology, China

Low temperature nitriding of Fe-Cr-Ni austenitic stainless-steel forms a nitrogen supersaturated layer that owns a composite property of wear and corrosion resistance. It is widely used in the industry, and nuclear power plant is a very important application for its stringent performance requirements. To understand the nature of this nitrogen supersaturated layer, a serial systematically composition changed Fe-Cr-Ni austenitic stainless steel in three groups are prepared, nitrided and investigated. It is confirmed that the nitrided layers on all the Fe-Cr-Ni austenitic alloys are consistent of duplex structure of outer γ -Fe N like orderedγ'_N and inner γ_N, althougha featureless continuous layer is observed with light-optical microscopy and a gradual decrease in nitrogen content is measured with EPMA when the alloys with a Cr-content over 12 wt. %. Cell model based on Cr-N and Fe-N interaction that considered the atomic construction of octahedral interstice is built that can explain the composition and structure evolution during the alloy composition change. The Cell Model is also used to calculated the average nearest neighbor nitrogen atoms (ANNNA) around Cr and Fe, which well explained the extended X-ray absorption fine structure (EXAFS) experiment results in both as nitrided and denitrided of 304 and 316 stainless steel. It further confirmed the reasonability of Cell Model and revealed the atomic structure of the γ'_N and γ_N phase.

AS-ThP-8 Determination of the Number of Layers of a 2D Material by Angle-Resolved Photoelectron Spectroscopy*, P Tyagi,* University at Albany - SUNY*; **Carl A. Ventrice, Jr.**,* SUNY Polytechnic Institute

The electronic structure of most 2D materials depends on the number of molecular layers and the stacking sequence between the layers. Therefore, it is important to have a non-destructive technique for analyzing the overlayer coverage of a 2D material directly on the growth substrate. A technique for determining the number of molecular layers using angle-resolved XPS has been developed. The system that will be presented is graphene growth on CuNi substrates, where controlled growth of multilayer graphene films can be performed. Since single atomic layer graphene films can be grown on Cu substrates, these samples are used as a standard reference for a monolayer of graphene. HOPG is used as a standard reference for bulk graphite. The electron mean free path of the C-1s photoelectron can be determined by analyzing the areas under the C-1s peaks of monolayer graphene/Cu and bulk graphite. With the electron mean free path, the graphene coverage of a film of arbitrary thickness can be determined by analyzing the area under the C-1s of that sample. In principle, this technique can be used to determine the thickness of other 2D materials if a sample with a single molecular layer can be prepared.

AS-ThP-9 Effect in Core Level Binding Energy Spectra of Phthalocyanine (MePcs) Functionalized Carbon Nanotubes Studied by XPS and DFT*, **Lázaro Huerta**,* Instituto de Investigaciones en Materiales, México*; E Basiuk, V Basiuk,* Universidad Nacional Autonoma de México, México*; R Escamilla,* Universidad Nacional Autónoma de México, México*; M Flores,* Universidad de Guadalajara, México, Mexico

In this work was studied single-walled carbon nanotubes (SWNT) functionalized with noncovalently bonded hybrids of 3d transition metal (Me) phthalocyanines MePcs by X-ray photoelectron spectroscopy (XPS) and density functional theory (DFT).

The transition metal Me 2p core level spectra exhibit a series of details, specifically shake-up and multiplet splitting. This latter can affect BE values for an electron from any orbital, as occurs in the links of the phthalocyanines under study, before and after interacting with the surface of the wall single-walled carbon nanotubes, in which not only the splitting occurs but, literally, bonds disappear, although its physical-chemical meaning is that its energy becomes indistinguishable.

The approximate XPS spectra measurements for neat MePcs (where Me=Co, Ni, Cu and Zn). and MePc+SWNT hybrids show very strong interactions between macrocyclic complexes and carbon nanotube sidewalls and found the existence of one N 1s component for noncovalent MePc+SWNT complexes versus three components for neat phthalocyanine β-polymorphs. As well the decrease of multiplet splitting and the increase of spectral resolution, observed for both N 1s, C 1s and Me 2p peaks as a result of phthalocyanine deposition onto SWNTs.

Density functional theory (DFT) studies, showed high absolute values of binding energies and show that the macrocycles (of MePcs) suffer strong bending distortion in order to increase the area of their contact with nanotube sidewall. The combination of XPS and DFT helps the final explanation.

AS-ThP-10 Probing the Electrical Double Layer by *in situ* X-ray Photoelectron Spectroscopy through a Carbon Nanotube-Strengthened Graphene Window*, P Wang, **Yunfeng Li**, L Wang, J Klos, Z Peng, N Kim,* University of Maryland, College Park*; H Bluhm,* Lawrence Berkeley National Laboratory*; K Gaskell, S Lee, B Eichhorn, Y Wang,* University of Maryland, College Park

A detailed description of the electrical double layer structure formed at the electrode-electrolyte interface is very important for both fundamental understanding in many electrochemical processes and further advancements in energy storage devices. However, the electrical double layer is deeply "buried" by the bulk electrolyte solution, leading to significant signal loss and low detection resolution when measuring the interface structure from the electrolyte side. Here, we report the fabrication of a novel transparent electrode made of a graphene-carbon nanotube hybrid membrane that allows us to detect the electrical double layer from the solid side of the electrode using X-ray photoelectron spectroscopy. The robust and ultrathin nature of the hybrid membrane enables the detection of different elements with excellent photoelectron signals. By *in situ* monitoring the concentration changes of cations and anions under different local electrical potentials, we experimentally decipher the chemical structure of the electrical double layer, which is consistent with theoretical predictions.

AS-ThP-11 Antibacterial Performance of Electrically Activated Conductive Water Filter Papers*, **Dorina Mihut**, A Afshar, L Lackey,* Mercer University

Silver and copper thin films were coated on commercially available 3 M water filter papers using DC high vacuum magnetron sputtering technique. The filter papers (10 X 7 cm size) are flexible structures consisting of nonconductive fibers and metallic nanoparticles were deposited with 300 nm and 1 µm thicknesses resulting in a complete coverage of the fibers surface. Both silver and copper thin films deposited on water filter paper are effectively working against common types of harmful bacteria that are found in waste water. The research is investigating the possibility of creating electrically conductive structures and the synergistic antibacterial effect obtained by using metallic thin films deposited on water filter paper and an electrical current applied to the structures. The antibacterial activity of electrically conductive structures was tested by applying an increased electrical potential. The morphology of the coatings and their adherence to the water filter paper was examined using the digital optical microscopy and Scanning Electron Microscopy and their chemical composition was investigated using the X-ray diffraction technique. A ll thin films showed good adhesion to water filter fibers and ensured a high area of exposure to contaminated water. The antibacterial effect of different conductive thin films was characterized by using the standardized membrane filtering technique for water and wastewater examination. The testing media (i.e. contaminated water) containing bacterial samples were collected from local wastewater basins. Water was tested for the bacterial content before and after the exposure to conductive thin films coated filters.

AS-ThP-12 Biocompatible and Robust Non-wetting Surface Inspired by Three Natural Organisms: Lotus Leaf, Mussel, and Sandcastle Worm*, **Kiduk Han**,* POSTECH, Republic of Korea*; T Park,* POSTEC, Republic of Korea*; H Cha, K Yong,* POSTECH, Republic of Korea

When the contact angle of water to a specific surface exceeds 150°, the surface is referred to as superhydrophobic (SH) surface. This SH surface has been developed by mimicking the Lotus leaf structure and it is useful for preventing structural deformation, oxidation and contamination of materials that can be affected by water. However, the SH surface has a limitation in practical use due to its poor physical durability, and there has been a great difficulty in applying it to research fields such as medical and tissue engineering due to the biohazard of its components. To overcome these problems, we have developed a technique for producing biocompatible and robust SH surfaces using mussel adhesive-protein adhesive (iMglue), and have applied this technology to catheters and patches to confirm its biomedical utility. The nanoparticles were deposited on the iMglue by dip coating and spray coating method, and the surface energy of the particles was lowered through chemical reaction to produce a water repellent surface. This surface is expected to play an important role in biomedical field due to its antibacterial and wound closure capabilities.

AS-ThP-13 In-situ ToF-SIMS Analysis of FIB Prepared Li Ion Battery Anodes*, **Vincent Smentkowski**, R Hart, H Cao,* GE-Research*; F Kollmer, J Zakel, H Arlinghaus,* IONTOF GmbH, Germany

Depth profiling (1D or 3D) is often used to determine the depth distribution of species in a material. Depth profiling works well when the surface of a sample is smooth and when the depth(s) are in the nm to micron thickness range. For thicker layers, one can mount the material in epoxy and generate a cross section which can be imaged. Unfortunately, cutting and polishing often damages (or at least smears) fragile materials such Li ion batteries. Over the two past decades, Focused Ion Beam (FIB) has proven to be a viable approach to expose sub surface layers 10s of microns thick which is often analyzed by SEM or TEM in conjunction with EDS [1]. Unfortunately, most EDS detectors are not able to detect light species such as Li and C (especially at the degraded vacuum which most SEM's operate under), and definitely can not detect H. ToF-SIMS not only detects all elements (and their isotopes), it also allows for the analysis of molecular fragments which is often critical for understanding the material. FIB/ToF-SIMS has been used to analyze other material systems [2, 3].

In this late breaking poster, we will provide preliminary in-situ FIB/ToF-SIMS results which were generated on an anode taken from a Li ion battery. In order to simultaneously obtain high lateral resolution images at high mass resolution, the delayed extraction data collection mode was utilized [4]. The advantages of multivariate statistical analysis (MVSA) for these complex data sets will be demonstrated.

[1] Lucille A. Giannuzzi, and Fred A. Stevie, Eds., "Introduction to Focused Ion Beams", Springer-Verlag US (2005) DOI: https://doi.org/10.1007/b101190.

[2] Felix Kollmer, D. Rading, R. Moellers, H.-G. Cramer, Wolfgang Paul, Ewald Niehuis, "Novel Cluster Ion Beams For Secondary Ion Generation, Sputtering And FIB/SIMS Application", Microscopy and Microanalysis 18(S2) (2012) 904-905; DOI: 10.1017/S143192761200637X.

[3] John S. Hammond, Gregory L. Fisher, Scott R. Bryan, Rait Kanarbik and Pritt Möller "FIB-TOF Tomography of Solid Oxide Fuel Cells", Microscopy and Microanalysis 19 (suppl 2) (2013) 672-673, DOI:10.1017/S1431927613005357.

[4] Quentin P. Vanbellingen, Nicolas Elie, Michael J. Eller, Serge Della-Negra, David Touboul, Alain Brunelle, "Time-of-flight secondary ion mass spectrometry imaging of biological samples with delayed extraction for high mass and high spatial resolutions" Rapid Commun. Mass Spectrom. 29 (2015) 1187–1195, DOI: 10.1002/rcm.7210

AS-ThP-14 Characterization of Surface-Immobilized Aptamers for Electrochemical Biosensing*, **Ramya Vishnubhotla**,* National Institute of Sandards and Technology (NIST)*; S Robinson, J Giddens,* University of Maryland, College Park*; S Semancik,* National Institute of Standards and Technology (NIST)

Electrochemical measurements have shown promise for detecting biomolecules such as DNA and proteins. In this presentation, we focus on surface-immobilized DNA aptamers that can be used to bind certain species and thereby produce electrochemical signals indicating detection of desired targets. Our sensing approach is based on monitoring binding events and conformation changes that occur on reusable, temperature-controlled electrochemical microdevices. We present our findings on two "model" aptamers that bind streptavidin and platelet-derived growth factor (PDGF), respectively. The commercially-purchased aptamers were bound to the Au working electrodes of the devices through a thiol group that was synthesized at the 5' end of the DNA. Changes in temperature caused folding and unfolding of the aptamer, altering the average distance between a terminal redox-active methylene blue moiety (at the 3' end) and the Au surface. The resulting change in current (due to electron transfer between each methylene blue molecule and the Au surface) was monitored over a temperature range of ~10 ^{o}C – 60 ^{o}C. Initial studies included surface characterization using XPS and AFM in order to better understand the behavior of the aptamers under environmental stressing, such as changes in the chemical environment and temperature. Surface plasmon resonance (SPR) studies were also performed to provide instrumental analyses of the aptamer-protein binding events, to compare to results obtained with the electrochemical microdevices.

Chemical Analysis and Imaging Interfaces Focus Topic
Room A226 - Session CA+AS+NS+SE+SS-FrM

Novel Applications and Approaches in Interfacial Analysis

Moderators: Paul Dietrich, SPECS Surface Nano Analysis GmbH, Germany, Jeong Young Park, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea

8:20am **CA+AS+NS+SE+SS-FrM-1 Chemical Reactions on Bimetal Surfaces with Operando Surface Techniques*, Jeong Young Park,*** Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea **INVITED**

The origin of the synergistic catalytic effect between metal catalysts and reducible oxide has been debated for decades. Clarification of this effect, namely the strong metal–support interaction (SMSI), requires an understanding of the geometric and electronic structures of metal–metal oxide interfaces under operando conditions.[1] A bimetallic platinum (Pt) alloy catalyst is an excellent platform to uncover the contentious role of the metal–metal oxide interface because the alloyed transition metal can coexist with the Pt surface layer in the form of an oxidized species on the bimetal surface during catalytic reactions.

In this talk, I present in-situ observation results of structural modulation on Pt-Ni metastable and Ni (111) surfaces at 0.1 Torr pressure of CO, O_2, and CO oxidation conditions with ambient-pressure scanning tunneling microscopy (AP-STM) and ambient-pressure X-ray photoelectron spectroscopy (AP-XPS).[2] We show that the stable Pt-skin covered Pt_3Ni(111) surface is broken by segregation of dissociative oxygen-induced Ni oxides under elevated oxygen pressure environment, which evolved clusters could have a crucial relation with enhanced catalytic activity. We show that NiO1-x/Pt-Ni nanostructures are on the Pt_3Ni(111) surface under CO oxidation and these metal-oxide interfaces provide more efficient reaction path for CO oxidation [2]. Furthermore, I will **show the research efforts for understand the catalytic behavior of bimetal PtCo and PtNi nanocatalysts using in-situ surface techniques including catalytic nanodiode and transmission electron microscopy. The catalytic nanodiode that consists of metal catalyst film, semiconductor layers, and Ohmic contact pads revealed the strong correlation between the hot electron flux (chemicurrent) and catalytic activity under CO oxidation and hydrogen oxidation. Using this approach, the catalytic activity and hot electron generation on PtCo bimetal nanoparticles were investigated. In-situ transmission electron microscopy reveals the formation of metal oxide layers on bimetal nanoparticle surfaces under oxygen conditions. We show that formation of interface between Pt and CoO enhances both of catalytic activity and chemicurrent yield [3].**

[1] J. Y. Park et al. Chemical Reviews 115, 2781-2817 (2015)

[2] J. Kim et al. Science Advances 4, eaat3151 (2018).

[3] H. Lee et al. Nature Communications 9, 2235 (2018).

9:00am **CA+AS+NS+SE+SS-FrM-3 Principal Component Analysis to Reveal Camouflaged Information in Spectromicroscopy of (complex) Oxides*, David Mueller,*** *M Giesen,* Forschungszentrum Juelich GmbH, Germany*; D Stadler,* University of Cologne, Germany*; T Duchon, F Gunkel, V Feyer,* Forschungszentrum Juelich GmbH, Germany*; S Mathur,* University of Cologne, Germany*; C Schneider,* Forschungszentrum Juelich GmbH, Germany

Spectroscopic imaging techniques are becoming more and more accurate and available, which results in an increase of data to handle and analyze. Near Edge X-Ray absorption spectroscopy, especially in the soft X-Ray regime, has the ability to identify inhomogeneities in chemistry and electronic structure, which is mostly done by fingerprinting or using internal standards. In a spectromicroscopic image, each pixel contains such a spectrum, and by the lack of rigorous fitting routines that are for example present in XPS, reduction and preevaluation of data is needed. Principal Component Analysis (PCA) of X-PEEM data affords this in an unambiguous and unbiased way by identifying and highlighting spectroscopic features which contribute to a spectrum.^{1}

Two cases where PCA revealed information that might have been missed otherwise are presented here: Firstly, iron oxide thin films grown by CVD showed a considerable influence of an external magnetic field on chemistry and crystallinity. Combination of O-K- and Fe-L-Edge X-PEEM unambiguously identified different iron oxide polymorphs (Fe_3O_4 and α-Fe_2O_3) depending on field strength during deposition. The former XAS Edge showed subtle spatial variations in the EXAFS regime that could be identified as the breakdown of long-range ordering, pointing to incomplete crystallization when films are deposited without magnetic field assistance.^{2}

The second example is the surface decomposition of $Pr_{0.5}Ba_{0.5}CoO_{3-\delta}$ (PBCO), a promising material for the use as water splitting catalyst and solid oxide electrochemical cell electrode. Using spatially resolved O-K-, Co-L-, and Ba- and Pr-M-Edge XAS, changes in surface chemical composition upon annealing and its impact on the electronic structure were observed. Laterally resolved by X-PEEM, PCA could reveal that exposing thin films of the material to technologically relevant conditions (1073 K, 20 mbar of O_2) leads to a more complex decomposition pathway than simple spinodal unmixing to the end members $BaCoO_3$ and $PrCoO_3$ as the spectromicroscopic dataset could only be described satisfactory by a linear combination of three components.

9:20am **CA+AS+NS+SE+SS-FrM-4 *In situ* Electron Microscopy of Catalysts with Atomic Resolution under Atmospheric Pressure*, Xiaoqing Pan,*** University of California Irvine **INVITED**

Understanding the atomic structures of catalysts under realistic conditions with atomic precision is crucial to design better materials for challenging transformations. For example, under reducing conditions, certain reducible supports migrate onto supported metallic particles and create strong metal−support states that drastically change the reactivity of the systems. The details of this process are still unclear and preclude its thorough exploitation. In the past decade, most of atomic-scale transmission electron microscopy (TEM) studies involving gas-solid interactions were conducted in an environmental TEM, where the gas pressure is typically limited to less than 1/100 of atmosphere. Recently, it has become possible to overcome this limitation through a MEMS-based, electron-transparent closed cell with a heating stage.

In this talk, I will present our recent results using this device (the Protochips Atmosphere^{TM}system) in selected catalyst systems. In a palladium/titania (Pd/ TiO_2) catalyst, we directly observed the formation of the oxide overlayers on the supported Pd particles with atomic resolution under atmospheric pressure and high temperature. It shows that an amorphous reduced titania layer is formed at low temperatures, and that crystallization of the layer into either mono- or bilayer structures is dictated by the reaction environment. This transition occurs in combination with a dramatic reshaping of the metallic surface facets. *In-situ*TEM observations of a modular Pd-ceria core-shell nanostructured catalyst (Pd@CeO_2) showed that an unexpected structural transformation occurs upon heating at high temperatures. The system reaches to a stable state with the mixture of nanoparticles with two different sizes, which accounts for the exceptional catalytic properties that have been reported. Using the similar techniques, we also studied the core-shell platinum-metal (Pt-M) nanoparticles which show a catalytic performance in the oxygen reduction reaction (ORR) superior to that of pure Pt nanoparticles. To understand the formation mechanism of the Pt shell, we studied thermally activated core-shell formation in Pt_3Co nanoparticles via *in-situ*electron microscopy with the gas cell. The disordered Pt_3Co nanoparticle was found to transform into an ordered intermetallic structure after annealing at high temperature (725°C) in 760 Torr O_2, followed by layer-by-layer Pt shell growth on (100) surfaces at low temperature (300°C). The apparent‘anti-oxidation’phenomenon promoted by the ordered Pt_3Co phase is favorable to the ORR catalyst, which operates in an oxidizing environment.

10:00am **CA+AS+NS+SE+SS-FrM-6 Exposing Buried Interfaces in Thin Film Photovoltaics through Thermo-mechanical Cleaving*, Deborah McGott,*** Colorado School of Mines*; C Perkins, W Metzger,* National Renewable Energy Laboratory*; C Wolden,* Colorado School of Mines*; M Reese,* National Renewable Energy Laboratory

Thin film solar cells, such as cadmium telluride (CdTe) and Cu(In,Ga)Se_2 (CIGS), contain buried interfaces that are critical to carrier transport, recombination, and device performance, yet are poorly understood due to their inaccessibility within the device stack. In particular, accessing the interface in a way that preserves the chemical structure has historically been extremely difficult. Here, we describe an innovative technique to expose buried interfaces through a two-step thermo-mechanical cleaving process. First, a stressor layer (typically an epoxy or commercially available polymeric backsheet) is applied to the solar cell. Then, the stack is submerged in a cold bath (T ≤ -30˚C) to thermally shock the system. This causes the stressor to contract quickly and pull the polycrystalline film cleanly off of its substrate at an interface that is weakened by a monolayer accumulation of 2-D material ($CdCl_2$ in CdTe and MoS_2 in CIGS) .

Focusing on CdTe solar cells, we then use X-ray photoelectron spectroscopy to probe the oxidation states at the newly exposed SnO_2 interface. We show that the tin oxide front electrode promotes the formation of nanometer-scale oxides of tellurium and sulfur. Most oxidation occurs during $CdCl_2/O_2$ activation. Surprisingly, we show that relatively low-temperature anneals (180−260°C) used to diffuse and activate copper acceptors in a doping/back contact process also cause significant changes in oxidation at the front of the cell, providing a heretofore missing aspect of how back contact processes can modify device transport, recombination, and performance. Device performance is shown to correlate with the extent of tellurium and sulfur oxidation within this nanometer-scale region. Mechanisms responsible for these beneficial effects are proposed.

10:20am **CA+AS+NS+SE+SS-FrM-7 Switchable Dopants on Percolation Networks of 2D Materials for Chemiresistive Sensing Applications in Aqueous Environments*, Peter Kruse,*** McMaster University, Canada

Permanent doping of semiconductors and low-dimensional structures to modulate their electronic properties is a well-established concept. Even in cases where doping of thin films by analytes (e.g. carbon nanotubes by ammonia) is applied in sensors, it is only reversed by physical removal of dopant molecules, e.g. heating. We have introduced the concept of molecular switches as chemical dopants for thin nanocarbon (or other 2D-materials) films. These molecules can be switched between doping and non-doping states in the presence or absence of a particular analyte. They impart selectivity not only due to their change in doping behavior, but also by physically blocking other potential dopants in the analyte solution from interacting with the conductive film. The resulting structures can act as chemiresistive films. Chemiresistive sensors are a well-established technology for gas-phase sensing applications. They are simple and economical to manufacture, and can operate reagent-free and with low or no maintenance. Unlike electrochemical sensors they do not require reference electrodes. While in principle they can be made compatible with aqueous environments, only a few such examples have been demonstrated. Challenges include the need to prevent electrical shorts through the aqueous medium and the need to keep the sensing voltage low enough to avoid electrochemical reactions at the sensor. We have built a chemiresistive sensing platform for aqueous media. The active sensor element consists of a percolation network of low-dimensional materials particles that form a conducting film, e.g. from carbon nanotubes, pencil trace, exfoliated graphene or MoS_2. The first member of that platform was a free chlorine sensor. We are currently working to expand the applicability of our platform to other relevant species, in particular anions and cations that are commonly present as pollutants in surface and drinking water. Our sensors can be incorporated into a variety of systems and will also be suitable for online monitoring in remote and resource-poor locations.

10:40am **CA+AS+NS+SE+SS-FrM-8 Analysis Of Radioactive Materials In Liquid Using In Situ Sem And Tof-Sims*, Jennifer Yao,*** *X Yu, Z Zhu, E Buck,* Pacific Northwest National Laboratory

Characterization of nuclear materials in solid particles or particles in liquid slurry, particularly in high level waste, can establish the elemental, organic, and isotopic compositions that effect the properties of the materials during nuclear fuel cycle activities and processes. Techniques to evaluate such detailed information, even at small concentrations, can support nuclear materials and science programs by increasing our ability to manage and control nuclear materials. However, radioactive materials analysis in liquids and slurries can be challenging using bulk approaches. We have developed a vacuum compatible microfluidic interface, system for analysis at the liquid vacuum interface (SALVI), to enable surface analysis of liquids and liquid-solid interactions using scanning electron microscopy (SEM) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). In this work, we illustrate the initial results from the analysis of liquid samples of importance in the geologic disposal of UO2 spent nuclear fuel in a repository environment using in situ liquid SEM and SIMS. Our results demonstrate that multimodal analysis of UO2 materials is possible using SALVI. Both in situ liquid SEM and SIMS can be used as new approaches to analyze radioactive materials in liquid and slurry forms of high level nuclear waste.

11:00am **CA+AS+NS+SE+SS-FrM-9 Interactions between Synthetic Bilgewater Emulsion and Biofilms*, Jiyoung Son,*** Earth and Biological Sciences Directorate*; J Yao,* Earth & Biological Sciences Directorate*; X Yu,* Pacific Northwest National Laboratory

Presentation Summary:

This presentation will showcase our latest results of the interaction between biofilms and synthetic bilgewater using a surface chemical imaging technique.

Abstract

Bilgewater, an oil-in-water (O/W) emulsion, is a persistent pollutant released to the ocean from the lowest part of ships. Microbes play an important role in the ocean. It is hypothesized that microbes release organics that can act as surfactants that affect bilgewater formation or weakening. We present the first systematic study of emulsions and biofilms and investigate the effects of biofilms on bilgewater emulsions. Three strains were selected *Pseudomonas*, *Arthrobacter*, and *Cobetia marina*. A Navy O/W emulsion consisting of three oils and a detergent mixture was used as the synthetic bilgewater model [1]. Biofilms were cultured in a microchannel to allow healthy culture [2]. Once a thick layer of biofilms was formed, the medium solution was changed to a mixture consisting of 50 % bilgewater emulsion. Dispersed biofilms were collected at 24 hrs. and 48 hrs. after emulsions were introduced into the channel. Bilgewater emulsions, biofilms, and mixtures of bilgewater emulsions and biofilms were analyzed using multiple *in situ* and *ex situ* techniques including time-of-flight secondary ion mass spectrometry (ToF-SIMS), scanning electron microscopy (SEM), and optical microscopy. Our findings indicate that biofilms change the chemical makeup of the emulsion surface compositions and emulsion droplet size distribution, confirming the hypothesis that extracellular polymeric substance (EPS) related components released from biofilms can function as surfactants and change the oil-in-water interfaces.

Key words: bilgewater emulsion, oil-in-water, microfluidics, biofilm, EPS, surfactant

Reference

1. Church, J., D.M. Paynter, and W.H. Lee, *In Situ Characterization of Oil-in-Water Emulsions Stabilized by Surfactant and Salt Using Microsensors.* Langmuir, 2017. **33**(38): p. 9731-9739.

2. Yao, J., et al., *In Situ Characterization of Boehmite Particles in Water Using Liquid SEM.* J Vis Exp, 2017(127).

11:20am **CA+AS+NS+SE+SS-FrM-10 Mechanistic Insights into the Study of γ -Al_2O_3 Surface and its Interface with Pt*, Kofi Oware Sarfo,*** *A Clauser, M Santala, L Árnadóttir,* Oregon State University

Metal/metal oxide interfaces occur in heterogeneous catalysis where metal catalyst nanoparticles are dispersed on highly porous metal oxide supports to increase the surface area for reactions. The interactions between catalyst nanoparticles and the catalyst support has previously been shown to affect the extent of dispersion of the active metal catalyst, particle sintering and the electronic properties of the catalyst. The capability to describe and predict the structure of the catalyst, the catalyst support and the interface between the two is therefore a critical step towards understanding the catalyst-support interactions. γ-Al_2O_3, a polymorph of Al_2O_3 is a commonly used catalyst support due to its durability at operation conditions and high surface area. Here we combine theoretical and experimental methods to investigate and predict the structure and thermodynamic stability of the interface between γ-Al_2O_3 and Pt nanoparticles. The experimental approach involves the fabrication of the embedded Pt nanoparticles and the use of high resolution transmission electron microscopy (HRTEM) to image the atomic structure for the embedded interfaces. The theoretical approach utilizes density functional theory (DFT) and thermodynamic models to calculate surface energies of γ-Al_2O_3 (111) and interfacial energies between Pt(111) and γ-Al_2O_3 (111) to describe the stabilities of the surfaces and interfaces. Of the three interfacial terminations, Pt atoms interacting with oxygen terminated γ-Al_2O_3 (111) are the most stable interfaces at atmospheric conditions. The stability of this interface is based on the strong electrostatic interaction between the Pt atoms and the oxygen atoms at the oxygen terminated interface. This work therefore, provides the complement to experimental study of the atomic structure of the interface between γ-Al_2O_3 and Pt nanoparticles.

11:40am **CA+AS+NS+SE+SS-FrM-11 Artificial Intelligence--An Autonomous TEM for In-situ Studies*, Huolin Xin,*** University of California Irvine **INVITED**

Deep learning schemes have already impacted areas such as cognitive game theory (e.g., computer chess and the game of Go), pattern (e.g., facial or fingerprint) recognition, event forecasting, and bioinformatics. They are beginning to make major inroads within materials science and hold considerable promise for materials research and discovery. In this talk, I will introduce deep convolutional neural networks and how they can be applied to the computer vision problems in transmission electron microscopy. I will also discuss the development and application of liquid TEM to the study of solid/liquid interfaces at the nanoscale.

Nanometer-scale Science and Technology Division
Room A222 - Session NS+AS-FrM

Electron-Beam Promoted Nanoscience

Moderators: Omur E. Dagdeviren, Yale University, Qing Tu, Northwestern University

8:20am **NS+AS-FrM-1 Vibrational Spectroscopy in the Electron Microscope***, **Ondrej Krivanek**, N Dellby, C Meyer, A Mitelberger, T Lovejoy,* Nion Co. **INVITED**

Vibrational (phonon) spectroscopy using an electron microscope's primary beam was introduced in 2014, and it has now progressed very significantly. The attainable energy resolution stands at ~5 meV (at 30 keV primary energy), our understanding of the electron-matter interaction has deepened, and several types of new applications have been explored.

Phonons can be excited by fast electrons in two fundamentally different ways: by dipole scattering, which is similar to exciting the sample by infrared light, and by impact scattering, which bears a closer resemblance to neutron scattering. Dipole scattering occurs only in polar materials, and it is characterized by small scattering angles (~0.1 mrad) and interaction distances of tens of nanometers. Impact scattering involves a direct interaction between the fast electron and an atomic nucleus, and it leads to large scattering angles. Selecting the impact scattering (with an aperture in the diffraction plane) allows the vibrational signal in h-BN to be imaged with atomic (0.2 nm) resolution [1,2]. In elemental Si, impact scattering is dominant, and it allows atomic resolution to be reached without angular selection [3].

The angular (momentum) distribution of vibrational scattering has also been explored [4-6]. Attainable spatial resolution is then inversely related to the angular resolution. Optical and acoustic branches of vibrational scattering have been mapped in hexagonal and cubic BN, and in graphene and graphite.

Dipole scattering provides another exciting possibility: probing the sample from a small distance, by "aloof spectroscopy". This approach limits the maximum energy that can be transferred to the sample with significant probability as 1/b, where b is the distance of the confined electron beam from the sample. In this way, vibrational properties of biological and other "fragile" materials can be probed without significant radiation damage [7], and this may well revolutionize analysis in the electron microscope. The technique has recently been used to detect isotopic substitution: ^{13}C vs. ^{12}C at a specific site in an amino acid (L-alanine), and to map the distribution of the two species [8].

[1] C. Dwyer et al., Phys. Rev. Letts **117** (2016) 256101

[2] F.S. Hage et al., Phys. Rev. Letts **122** (2019) 016103

[3] K. Venkatraman et al., arXiv:1812.08895 (2018)

[4] F.S. Hage et al., Sci. Adv. 2018;4:eaar7495 1-5

[5] R. Senga et al., arXiv:1812.08294 (2018), Nature (2019, in print)

[6] Lovejoy et al. Proceedings 2019 M&M Conference (in print)

[7] P. Rez et al., Nature Comms **7** (2016) 10945, doi: 10.1038/ncomms10945

[8] J. Hachtel et al., Science **363** (2019) 525–528

9:00am **NS+AS-FrM-3 In-situ Electron Microscopy of Localized Surface Plasmon Initiated Reactions***, **Canhui Wang**, W Yang, A Bruma,* UMD/NIST*; R Sharma,* National Institute of Sandards and Technology (NIST) **INVITED**

Excitation of localized surface plasmon (LSP) resonance on metal nanoparticles has been shown to overcome the reduced the energy barrier for photochemical reactions, even allowing certain reactions to occur at room temperature. (1-2) Understanding the reactions promoted by LSP resonance at the nanoscale is important for designing efficient photocatalytic systems for a wide range of energy and environmental applications. However, many important questions related to this type of reaction process remain unclear due to the complexity of the reaction kinetics, and lack of spatial resolution available with optical methods. Details such as the location of gas adsorption sites, how the energy is being absorbed and released, and how those details are correlated to the structure of the catalyst nanoparticles, remain elusive and are only hinted by theoretical calculations.

Here we use *in-situ* electron microscopy and combine an ensemble of data acquisition and processing techniques to characterize LSP-initiated chemical reactions at high spatial resolution using an aberration-corrected environmental scanning transmission electron microscope. Electron energy loss spectrum (EELS) imaging is used to acquire both elemental and LSP resonance maps from the same area that contains the plasmonic nanoparticles. The elemental maps allow us to locate the gas adsorption sites, the elemental distribution of the reactants and plasmonic nanostructures, as well as the spatial distribution of the solid reaction products, with nanometer resolution. The LSP-EELS maps provide insight into how the energy is channeled from the fast electron to the plasmonic nanostructure. Localized reactant consumption (mass loss) distribution is mapped in terms of thickness changes by subtracting the thickness map acquired after the reaction from the thickness map acquired before the reaction. This allows us to pinpoint the reaction hotspot near the nanoparticle surface. The LSP induced electric field distribution near the nanoparticle surface is simulated using the metallic nanoparticles boundary element method(MNBPEM) (3) and compared with the reactant mass loss map. These techniques allow us to explore and study previously unknown LSP initiated reactions with unprecedented details on the sub-particle level. (4) The results improved the understanding of the dynamics of LSP initiated reactions and give insights into nanoparticle engineering for optimizing reaction efficiency.

1. Mukherjee S, et al. (2012) Nano letters 13(1):240-247.

2. Thomann I, et al. (2011) Nano letters 11(8):3440-3446.

3. Waxenegger. J, et al. (2015) Comp. Phys. Commun. 193, 138.

4. Yang, W.C.D, et al. (2019) Nature Mater. 1.

9:40am **NS+AS-FrM-5 Nanoscale Manipulation of Redox of Ag by Electron Beam***, **Jianguo Wen**, H Sheng,* Argonne National Laboratory*; J Wang,* Wuhan University, China **INVITED**

Employing electrons for direct control of nanoscale reaction is highly desirable since it provides fabrication of nanostructures with different properties at atomic resolution and with flexibility of dimension and location. In 2016, Kalinin et al summarized past experiments of manipulating atoms with scanning transmission electron microscopy (STEM) and proposed to utilize the imaging tool to create structures atom by atom (1). Here, applying *in situ* transmission electron microscopy, we show nanoscale oxidation and reduction of Ag can be manipulated by electron beam. We demonstrated fabrication of an array of 3 nm Ag_2O nanodots in an Ag matrix.

Under high vacuum environment (~10^{-7} Torr pressure), oxygen in a TEM can be ionized by high-energy electron beam and causes oxidization of Ag. After enough e-beam illumination, a growth of Ag_2O on the surface is observed when electron beam flux is below ~$5x10^5$ $e^-/Å^2s$. Ag_2O islands epitaxially grow on Ag surface with orientation relationship of $<110>_{Ag}$ // $<110>_{Ag2O}$ and $\{111\}_{Ag}$ // $\{002\}_{Ag2O}$ in most cases. In-situ high-resolution transmission electron microscopy (HRTEM) imaging shows that Ag_2O nucleates at atomic steps on Ag surfaces.

With the increase of electron-beam intensity above ~$5x10^5$ $e^-/Å^2s$, the formed Ag_2O islands can be fully reduced back to Ag, such that a fully reversible oxidation and reduction of Ag is achieved by varying electron beam intensity. The growth and reduction of Ag2O island is electron-beam dose rate dependent, a near equilibrium state has been achieved at the dose rate of ~$5x10^5$ $e^-/Å^2s$. A brief explanation for this electron-beam dose rate dependence is the competition between the electron-beam ionization induced oxidation of Ag and electron stimulated desorption induced reduction of Ag_2O. Aberration-corrected HRTEM observation reveals that O atoms are preferably inserted and extracted along the {111} close-packed planes of Ag, leading to the nucleation and decomposition of nanoscale Ag2O islands on the Ag substrate.

Taking another step further, patterned oxidation has also been tested to verify the reliability of the electron-beam irradiation as a nanofabrication technique. By controlling probe size, electron flux, and dwell time, we demonstrated fabrication of an array of 3 nm Ag_2O nanodots in an Ag matrix. These findings do not only facilitate the basic understanding of oxidation/reduction kinetics in Ag-Ag_2O, but also open up a promising approach for precise fabrication of nanostructures with metal or semiconductor properties in devices.

1) Kalinin, Sergei V., Albina Borisevich, and Stephen Jesse. "Fire up the atom forge." *Nature News* 539.7630 (2016): 485.

10:20am **NS+AS-FrM-7 Dynamics of Material Surfaces and Interfaces – The Good, the Bad and the Electron Beam***, **Jakob Birkedal Wagner**,* DTU Nanolab, Technical University of Denmark, Denmark **INVITED**

A good understanding of the dynamics and formation mechanisms of surfaces and interfaces at the nanometer scale is of great importance in order to exploit the controllability of nanostructures and their applications in photovoltaics, electronics, sensors, *etc.* on an industrial scale.

In situ electron microscopy serves a unique platform for monitoring and studying structural dynamics at length scales from micrometer down to atomic scale and temporal resolution approaching millisecond range. In addition, elemental and chemical information is gained from spectroscopic techniques with spatial resolution approaching the atomic scale.

Here, I will present a few cases of the surface and interface dynamics studied at the microscopy facility at Technical University of Denmark. This includes surface dynamics of supported nanoparticles (catalyst) [1] under harsh environment (elevated temperature, gas and electron beam), as well as interface dynamics of grain boundaries in metal thin films [2], growth of nanostructures from bottom-up processes [3-6] and volatility of soot oxidation catalysts. [7]

The influence of the high-energetic electron beam will also be discussed in terms of sample damage and controlled reaction enhancement.

References

[1] P. Liu, PhD thesis (2018), Technical Unity of Denmark

[2] A. Bastos Fanta *et al.* Materials Characterization 139, 452 (2018)

[3] J. Kling *et al.* Carbon 99, 261 (2016)

[4] L.. Zhang *et al*. ACS Nano 11, 4483 (2017)

[5] S. Rackauskas *et al.,* Scientific Reports 7, 12310 (2017)

[6] W. F. van Dorp *et al.*, Nanotechnology 24, 345301 (2013)

[7] D. Gardini *et al.*, Appl. Catal. B, 183, 28 (2016)

11:00am **NS+AS-FrM-9 Atomic-Scale Mechanism of Unidirectional Oxide Growth***, **Xianhu Sun**, W Zhu, D Wu,* SUNY Binghamton University*; Z Liu,* University of Pittsburgh*; X Chen, L Yuan,* SUNY Binghamton University*; G Wang,* University of Pittsburgh*; R Sharma,* National Institute of Standards and Technology (NIST)*; G Zhou,* SUNY Binghamton University

A fundamental knowledge of the unidirectional growth mechanisms is required for precise control on size, shape, and thereby functionalities of nanostructures. Using transmission electron microscopy that spatially and temporally resolves CuO nanowire growth during the oxidation of copper, here we provide direct evidence of the correlation between unidirectional crystal growth and bicrystal boundary diffusion. Based on atomic scale observations of the upward growth at the nanowire tip and oscillatory downward growth of atomic layers on the nanowire sidewall, we clearly show that bicrystal boundary diffusion is the mechanism by which Cu atoms are delivered from the nanowire root to the tip. Together with density-functional theory calculations, we further show that the asymmetry in the corner-crossing barriers promotes the unidirectional oxide growth by hindering the transport of Cu atoms from the nanowire tip to the sidewall facets. We expect broader applicability of our results in manipulating the growth of nanostructured oxides by controlling the bicrystal boundary structure that favors anisotropic diffusion for unidirectional, one-dimensional crystal growth for nanowires or isotropic diffusion for two-dimensional platelet growth.

11:20am **NS+AS-FrM-10 Application of Electron-beam-excited Localized Surface Plasmon Resonance to Provide Guidelines for Plasmonic Catalysts***, **Wei-Chang Yang**[1], C Wang, L Fredin, H Lezec, R Sharma,* National Institute of Standards and Technology (NIST)

Optically-excited localized surface plasmon (LSP) resonances have been used to induce chemical reactions, such as hydrogen dissociation and ethylene epoxidation. Energy harnessed by plasmonic nanostructures and transferred to adsorbed reactants is theorized to initiate these chemical processes by compensating for the heat required otherwise. As we know, there are three important steps for designing a plasmonic catalyst system: (1) adsorption of reactants; (2) adequate resonance energy to overcome the reaction barrier; and (3) desorption of products. However, they have not been resolved at a sub-nanoparticle scale using optical methods. Herein, we demonstrate that the sub-particle information, gained from electron energy-loss spectroscopy (EELS) and cathodoluminescence (CL), can be used to measure these steps for selected reactions.

LSP resonances, excited by electrons, on shape-controlled Au nanoparticles, were exploited to drive CO disproportionation: $2CO_{(g)}$ --> $CO_{2(g)} + C_{(s)}$, at room temperature (commonly initiated by heat above 400 ˚C) in an environmental scanning transmission electron microscope equipped with a monochromated electron gun. Triangular Au nanoprisms were synthesized and loaded on TiO_2 support in a cantilevered configuration. *In situ* core-loss EELS was used to detect CO adsorption on the Au surfaces, for the first time, revealing the preferential adsorption sites at selective edges but not on the entire surfaces. Low-loss EELS maps of the Au nanoprisms showed that the electron beam was most efficiently coupled with the LSP dipole mode, indicated by the maximum EELS intensity, when placed at the cantilevered corner, suggesting a strong electric field caused by this specific mode at the same corner. *In situ* EELS showed that energy shifts occurred to the LSP resonance in CO environment and disappeared after CO evacuation, indicating a change in electron density of the Au particle as CO was adsorbed and desorbed, respectively. Energy transferred to the adsorbed CO was identified based on the spectral difference between EELS and CL. Carbon deposits, resulting from room-temperature CO disproportionation mediated by the LSP resonance, were detected by core-loss EELS at the cantilevered corner edge after evacuating CO. This shows that the active sites on the nanoprisms are where the preferable CO adsorption sites and the locations of maximum field amplitude superimpose.

Our findings provide unprecedented information on an LSP-induced chemical reaction with nanometer precision, shedding light on the design principles for new plasmonic catalysts that enable low-temperature reactions.

Advanced Surface Engineering Division
Room A215 - Session SE+AS+SS-FrM

Tribology: From Nano to Macro-scale

Moderators: Robert Franz, Montanuniversität Leoben, Andrey Voevodin, University of North Texas

8:20am **SE+AS+SS-FrM-1 The Scaling of Tribological Effects from Nano- to Macro-scale***, **Peter Lee**,* Southwest Research Institute **INVITED**

The last few decades has seen the advancement of technologies such as atomic force microscopes (AFM), scanning force microscopes (SFM) and friction force microscopes (FFM) to measure friction, wear and adhesions at the nano- and micro-scale, leading to the study of nano- and micro-tribology. The study of two surfaces at the nano- and micro-meter scale has led to the advancement of small scale engineering devices such as nano- and micro-electromechanical systems (NEMS and MEMES). However, it has also led to the study of materials used in macro-engineering in an attempt to understand the fundamentals of lubrication, friction and wear at the asperity scale in macro-systems.

Macro-tribology involves large apparent areas of contact where only a fraction of the asperity tips are in contact, whereas nano-tribology usually involves studying a single asperity contact where the actual contact is the same as the apparent contact. Consequently, roughness and actual contact shape plays a more significant role in the tribological behavior, which in turn means significant effects on forces such as friction, adhesion and surface tension. Tribology at the macro-scale is governed by complex phenomena such as ploughing, abrasive, and adhesive wear. Friction at the nano-scale is often studied purely in the wearless (interfacial) regime, where adhesion is substantial but wear is minimal.

This presentation will explore current research at the nano-scale and discuss how this has the potential to help in understanding and modeling at the macro-scale.

9:00am **SE+AS+SS-FrM-3 Nanotribology of Graphene in Organic Solvents***, **Prathima Nalam**, B Sattari Baboukani,* University at Buffalo, State University of New York*; Z Ye,* Miami University

Two-dimensional (2D) materials such as graphene, *etc.* are emerging as friction-reducing additives for transmission fluids and lubricating oils to enhance the service life of sliding metallic components. Here in this work, we investigate the dissipative mechanism for a supported (on silica substrate), monolayer of graphene when immersed in organic solvents such as *n*-hexadecane and cyclohexane. Nanoscale friction measurements on graphene conducted using atomic force microscope showed a non-monotonic variation *i.e.* a decrease and then an increase in friction forces as a function of immersion time in organic solvents. This behavior was attributed to the re-arrangement of organic molecules at the 2D confinement formed between the graphene and the underlying substrate. The oscillatory forces measured at the interface showed an increased packing order of the solvent molecules under 2D confinement and with equilibration time lead to a higher dissipative interface. The diffusion of organic molecules to the 2D confinement also results in a partially-

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[1] **NSTD Early Career Award Finalist**

suspended graphene layer and the interfacial friction is discussed by understanding the quality (local pinning states of individual atoms) of the contact made by the AFM probe while sliding on graphene.

9:20am **SE+AS+SS-FrM-4 Measuring Atomicscale Surface Friction of a Molecular Vehicle on Au(111)***, K Latt,* ***Sanjoy Sarkar****, K Kottur, M Raeis,* Ohio University*; A Ngo,* Argonne National Laboratory*; R Tumbleson, Y Zhang, E Masson, S Hla,* Ohio University

Designing molecules with technomimetic properties has been actively pursued in the past decade. Among these, molecules specially designed for translational motion, dubbed as nanocars or molecular vehicles, are particularly appealing as they could ultimately be used to transport a molecular cargo or some specific chemical information from a start to an end point on a surface and on demand. Here, we have designed and assembled an electric nanovehicle using four molecular wheels and a molecular chassis as separate modules. An 'H' shape chasis is formed by two benzimidazolium groups linking the front and the rear axles to a terphenyl drive shaft. Final assembly of the nanovehicle is realized by attaching four pumpkin shaped cucurbituril molecular wheels. The chassis of the nanovehicle includes positive charges, which are used for the controlled lateral movement of the vehicle by scanning tunneling microscope tip induced electric field manipulation. The threshold voltage required to drive the nanovehicle is determined from the Vaussian-fit of the data. Moreover, we have determined lateral force to move the nanovehicle on a Au(111) surface at 5K and it is found to be in superlubricity regime.

9:40am **SE+AS+SS-FrM-5 The Use of the Nanocomposite Concept in Hard Coatings for Improving the Frictional Performance***,* ***Albano Cavaleiro,*** University of Coimbra, Portugal **INVITED**

Nanocomposite thin films based on a structural arrangement consisting of grains of a transition metal nitride enrobed in a thin layer of silicon nitride, have been developed in last decades with the final aim of maximizing the mechanical strength. This specific arrangement was proved to be efficient regarding the oxidation resistance and the structural stability at high temperatures as well as the wear resistance, reason why these coatings are commercially available in the market. However, their performance in applications requiring low friction, against specific materials, is very inefficient. On the other hand, in last years the addition of elements, able to provide low friction, such as Ag or V, to traditional hard coatings (TiN, TiAlN, TiCrN,…) has been deeply studied. Results were very successful from the lubrication point of view but the wear resistance was clearly reduced, due to either a decrease of the global mechanical strength of the coatings or the rapid depletion of the lubricant element from the coating by out diffusion to the contact zone.

In this talk an overview of the influence of the addition of lubricant elements to Ti-Si-N system will be presented. The coatings were deposited by conventional magnetron sputtering as well as by using HiPIMS power supplies. The importance of the type of the structure of the deposited coatings (nanocomposite or supersaturated solid solution) on their thermal stability, including oxidation resistance, will be discussed based on the diffusion of the lubricant elements. A comparison of the mechanical properties of the coatings deposited by both methods will be performed and the results will be interpreted based on the (micro)structure and residual stresses. Results on the tribological behaviour achieved by tests at room and high temperatures (up to 900 ºC) against different balls (steel, alumina and Ti-alloy) will be presented and commented. Generally, results show that a decrease of the mechanical performance of the coatings is obtained with that elements addition. However, in relation to tribological performance, significant improvements could be reached although under specific testing conditions (type of ball, temperature, …). In many cases, no improvements were observed.

10:20am **SE+AS+SS-FrM-7 Development of Ultra-thick CrAlAgN Coatings by HiPIMS for Self-lubrication at Elevated Temperatures***,* ***Jianliang Lin,*** Southwest Research Institute*; X Zhang,* Southeast University, China

The pursuit of advanced coating systems to provide sufficient oxidation resistance and self-lubrication for high temperature tribological application continues. One of the approaches is to dope traditional hard transition metal nitride coatings with solid lubricants, e.g. Ag, Au, which diffuses towards coating surface to provide lubrication at elevated temperatures. However, the long term performance of these self-lubricating coatings at high temperatures in ambient air is limited by the rapid out diffusion of Ag, which is strongly affected by many factors, e.g. the volume fraction of the dopant and the density of the coating. It is expected that dense coating structure combined with increased coating thickness is helpful for achieving long term lubrication performance. In this paper, ultra-thick CrAlAgN coatings (50 µm) are deposited on steel and cement carbide substrates using high power impulse magnetron sputtering (HiPIMS) by carefully control the processing parameters. The structure and composition of the coatings were first tailored to achieve a combination of good adhesion, high density and good mechanical strength with HiPIMS deposition. The Ag concentration in the coatings is varied in the range of 3-10 at.%. For the coating performance, the oxidation resistance of the coating were studied in ambient air using isothermal test. The high temperature wear resistance of the coating was measured using a high temperature pin-on-disc tribometer in the ambient air from 500 °C to 900 °C. It was found that Ag doping degrades the mechanical strength and oxidation resistance of the CrAlN coatings, but the ultra-thick CrAlAgN coating show robust self-lubricating performance at high temperatures.

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