Biomaterial Interfaces Division
Room B117-119 - Session BI2+AS+HC+SS-MoM

Energy Transfer and Light Induced Phenomena in Biologic Systems

Moderators: Morgan Alexander, University of Nottingham, UK, **Tobias Weidner**, Aarhus University, Denmark

10:40am **BI2+AS+HC+SS-MoM-8 Electrochemically Conducting Lipid Bilayers: Q-Lipid-Containing Membranes ShowHigh in-Plane Conductivity Using a Membrane-on-a-Chip Setup***, U. Ramach,* TU Wien, Austria*; J. Andersson,* IST Austria*; **Markus Valtiner,*** TU Wien, Austria

The light-driven reactions of photosynthesis as well as the mitochondrial powersupply are located in specialized membranes containing a high fraction ofredox-active lipids. In-plane charge transfer along such cell membranes iscurrently thought to be facilitated by the diffusion of redox lipids and proteins.

Using a membrane on-a-chip setup, we show here that redox-active model membranescan sustain surprisingly high currents (mA) in-plane at distances of 25 mm.Wealso showthe same phenomenon in free-standing monolayers at the air-waterinterface once the film is compressed such that the distance between redox centersis below 1 nm. Our data suggest that charge transfer within cell walls hostingelectron transfer chains could be enabled by the coupling of redox-lipids viasimultaneous electron and proton in-plane hopping, similar to conductive polymers.This has major implications for our understanding of the role of lipid membranes,suggesting that Q-lipid-containing membranes may be essential forevolving the complex redox machineries of life.

[1] U. Ramach, J. Andersson, R. Schöfbeck and M. Valtiner, Iscience 26 (2), 2023.

11:00am **BI2+AS+HC+SS-MoM-9 Light Responsive Cyclic Peptide Polymer Nanomaterials***, O. Atoyebi, M. Beasley, W. Maza, M. Kolel-Veetil, A. Dunkelberger, **Kenan Fears,*** US Naval Research Laboratory

Cyclic peptides are capable of self-assembling into supramolecular peptide nanostructures, via hydrogen bonding along the backbone of the peptide rings. To improve upon this molecular architecture, we designed and synthesized cyclic peptide polymers by covalently linking the cyclic peptides into a linear polymer chain, and demonstrated the conformation of the polymer chain could be transitioned from an unfolded state into rigid, peptide nanorods by varying solution pH. Here we present an alternate way to control the self-assembly via photo-isomerization. We capitalize on azobenzene's photo-actuable nature using a di-carboxylic acid azobenzene to covalently crosslink the cyclic peptide rings into a linear cyclic peptide polymer via terminal amines present in the ring. Self-assembly of the cyclic peptide nanotube occurs by exposing the polymerized cyclic peptide to ultraviolet radiation causing a trans- to -cis transition of the azobenzene and thus assembling the cyclic peptide nanotube. Furthermore, we fluorescence donor/acceptor pairs can be displayed from these materials, at highly controlled separation distances, to alter the optical response of these materials as a function of polymer conformation.

11:20am **BI2+AS+HC+SS-MoM-10 Programmable Biomimetic Light-Harvesting Systems based on Strong Coupling of Synthetic Peptides and Dye-Functionalised Polymer Brushes to Plasmon Modes***, **Graham Leggett**,* University of Sheffield, UK

Excitation transfer in molecular photonic materials is dominated by incoherent hopping processes; consequently, exciton diffusion lengths are short (~10 nm) placing severe constraints on device design. A grand challenge for the past two decades has been to discover how to achieve efficient long-range transfer of excitation in molecular systems. We have developed a new approach to the design of materials for solar energy capture that combines biomimetic design, inspired by structures used in photosynthesis, with strong light-matter coupling.

Photosynthetic pigment-protein light-harvesting antenna complexes (LHCs) from plants and bacteria are strongly coupled to the localised surface plasmon resonances (LSPRs) in arrays of metal nanostructures leading to the formation of macroscopically extended excited states. Modelling of data indicates that the coupling results from linear combinations of plasmon and exciton states. For example, wild-type and mutant LH1 and LH2 from *Rhodobacter sphaeroides* containing different carotenoids yield different coupling energies; the methods of synthetic biology enable strong light-matter coupling to be programmed.

However, proteins are not suitable for putative applications of molecular photonic materials. Instead, we have designed programmable biomimetic pigment-peptide and pigment-polymer antenna complexes, in which surface-grafted peptide and polymer scaffolds organise excitons within localised surface plasmon resonances to achieve strong light-matter coupling. In these systems, delocalised excited states (plexcitons) extend across at least 1000s of pigments. In synthetic peptide and protein systems, we find that the plasmon mode couples to states not seen under weak-coupling, providing evidence for the formation of macroscopically-extended excited states that facilitate coherent transfer of excitation across long distances. In pigment-polymer systems, the dye concentration in the film can be increased to ~2M, significantly exceeding the concentration of chlorophyll in biological light-harvesting complexes, by optimisation of the polymer grafting density and the dye-scaffold coupling chemistry. Fitting of spectra for these plexcitonic antenna complexes yields Rabi energies up to twice as large as those achieved with biological LHCs. Moreover, synthetic plexcitonic antenna complexes display pH- and temperature-responsiveness, enabling active control of strong plasmon-exciton coupling via regulation of the polymer conformation.

These biomimetic quantum-optical brush systems offer great promise for the design of new types of molecular photonic device.

Chemical Analysis and Imaging of Interfaces Focus Topic
Room A105 - Session CA1+AS+LS+NS+SS+VT-MoM

Modeling, AI, and Machine Learning Applied to Interfaces

Moderators: J. Trey Diulus, NIST, **Kateryna Artyushkova**, Physical Electronics

8:20am **CA1+AS+LS+NS+SS+VT-MoM-1 Topological and Geometric Descriptors of Complex Self-assembly at Liquid Interfaces***, **Aurora Clark,*** University of Utah **INVITED**

Amphiphilic surfactants at liquid/liquid interfaces can form complex self-assembled architectures that underpin interfacial reactivity and transport. This has been demonstrated by surface sensitive spectroscopies and molecular dynamics simulations within the domain of liquid/liquid extraction, which involves solute adsorption, complexation reactions and transport across the phase boundary. Being able to quantify surfactant organization is a significant challenge because the distribution of species is broad and highly heterogeneous. As such, in the analysis of molecular dynamics data, there is significant need to develop descriptors that allow statistical analysis of surface organization. This work presents recent developments based upon geometric measure theory and topological data analysis that are able to identify surface assemblies and their dynamic evolution. These methods are revealing intricate dependencies of surface assembly upon solution composition and the impact this has upon transport mechanisms.

References:

Kumar, N.; Clark, A. E. Persistent Homology Descriptors for Surface Image Analysis in Complex Chemical Systems, *Journal of Chemical Theory and Computation*, **2023**, *In Press.* ChemArXiv: https://doi.org/10.26434/chemrxiv-2023-vwrxj

Zarayeneh, N.; Kumar, N.; Kalyanaraman, A.; Clark, A. E. Dynamic Community Detection Decouples Hierarchical Timescale Behavior of Complex Chemical Systems, *Journal of Chemical Theory and Computation*, **2022**, *18,* 7043 – 7051. **DOI:**10.1021/acs.jctc.2c00454

Kumar, N.; Clark, A. E. Unexpected Inverse Correlations and Cooperativity in Ion-pair Phase Transfer, *Chemical Science,***2021**, *12,* 13930-13939.**DOI**: 10.1039/D1SC04004A

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Alvarado, E.; Liu, Z.; Servis, M. J.; Krishnamoorthy, B.; Clark, A. E. A Geometric Measure Theory Approach to Identify Complex Structural Features on Soft Matter Surfaces, *Journal of Chemical Theory and Computation*, **2020**, *16,* 4579-4587.**DOI:** 10.1021/acs.jctc.0c00260,

9:00am **CA1+AS+LS+NS+SS+VT-MoM-3 Machine Learning and the Future of Surface Analysis***, J. Jones, M. Caouette, **Kateryna Artyushkova,*** Physical Electronics **INVITED**

Machine learning can potentially revolutionize all areas of material science and engineering, including surface analysis, by automating and accelerating data acquisition and analysis. The application of machine learning and artificial intelligence (ML/AI) has been actively evaluated and used in scanning probe microscopic methods[1-2], while the application of AI in surface analysis methods such as AES, XPS, and TOF-SIMS is in the very early stages.[3] In this talk, I will discuss the potential areas where AI will change how we do surface analysis.

With recent instrumental development yielding improvements in sensitivity and throughput, the data acquisition stage of surface analysis has become much faster than the experimental planning or data analysis stages, which bothrequire significant operator time and human-based decisions. Using a spectrometer still requires a human operator with instrument-specific knowledge and experience in how to operate it. More importantly, the operator uses physical and chemical knowledge to decide on what specific data must be obtained and from which locations on the sample, depending on the analytical question being addressed by the experiment. Experienced scientists make these decisions effortlessly during the experiment, but it is a very challenging task for ML algorithms that rely on training data with explicit descriptors.

Initial AI applications to analytical surface analysis will focus on instrument optimization and performance inherent in the analytical workflow. Unlike acquisition parameters based on chemical or material science requiring broader context, tuning, and standardizing the spectrometer can be easily cast into numerical terms processable by AI.

Machine learning can also be utilized as a live data integrity monitoring service during acquisition, recognizing and rejecting "bad data". Systemically erroneous data caused by charging or sample damage are often not discovered until the experiment is complete and the data analyzed by a human. Catching it automatically during the experiment saves valuable operator and instrument time. Here, I will present an initial application wherein ML was used to identify whether ToF-SIMS spectra were correctly calibrated.

1.S.V.Kalinin, *ACS Nano*2021, 15, 8, 12604–12627.

2. S.V.Kalinin, arXiv:2304.02048

3. G Drera *et al* 2020 *Mach. Learn.: Sci. Technol.*1 015008

9:40am **CA1+AS+LS+NS+SS+VT-MoM-5 Complexity to Clarity: Detecting, Identifying and Analyzing Complex Materials with Machine Learning***, **Paul Pigram**, W. Gardner, S. Bamford, D. Winkler, B. Muir, R. Sun, S. Wong,* La Trobe University, Australia

Our ability to analyze and understand any physical, chemical, or biological material relies on accurately determining its structure, characteristics, and responses. Contemporary analytical techniques produce large volumes of data from pointwise sample analyses (one dimensional (1D) data), maps of compositional distributions (two dimensional (2D) data), and depth profiles showing composition throughout a sample volume (three dimensional (3D) data).

Correlative analyses linking data from the same sample, obtained by different analytical techniques or different operating parameters, are becoming critically important. Different analytical perspectives on the same sample enhance the richness and depth of the conclusions that can be drawn from it.

Recent advances in analytical science have resulted in an overwhelming avalanche of data – the "big data" problem. In our lab a single time-of-flight secondary ion mass spectrometry (ToF-SIMS) experiment might collect a map (512 x 512 pixels) with 2000 mass spectral peaks of significant intensity in 2 – 10 minutes. These half a billion data points all have differing degrees of significance.

In many cases, only a small number of peaks, 10 – 200, may be judged to be characteristic of a specific sample, and the rest of the data may be discarded. However, there are significant risks that such analyses are biased, and may miss important but subtle trends.

There is a very substantial knowledge gap in our ability to find and make full use of the information and knowledge contained in large scale data sets. This gap is driving rapid international progress in the application of materials informatics and machine learning to analytical surface science.

This presentation will highlight our work on applying artificial neural network approaches to analysis of a variety of very large hyperspectral data sets to better understand complex materials and their interactions.

Laboratory-Based Ambient-Pressure X-ray Photoelectron Spectroscopy Focus Topic
Room B116 - Session LX+AS+HC+SS-MoM

Laboratory-Based AP-XPS: Advances in Instrumentation and Applications

Moderators: Sylwia Ptasinska, University of Notre Dame, **Heath Kersell**, Oregon State University

8:20am **LX+AS+HC+SS-MoM-1 Instrumentation for Electron Microscopy and Spectroscopy in Plasma Environment***, **Andrei Kolmakov**,* NIST-Gaithersburg **INVITED**

Plasma-assisted processes are of principal importance for modern semiconductors microfabrication technology, catalysis, environmental remediation, medicine, etc. Understanding the chemical and morphological evolutions of the surfaces and interfaces under a plasma environment requires *operando* metrologies that have a high spatial, temporal, and spectroscopic resolution. Combining the APXPS system with ambient pressure scanning electron microscopy would, in principle, meet these needs. Here we review the status of the field and discuss the prospective designs as well as application examples of ambient pressure scanning electron microscopy and spectroscopy for *in situ* analysis and processing of the surfaces under plasma environments

9:00am **LX+AS+HC+SS-MoM-3 Scienta Omicron HiPPLab - A Lab-based APXPS Instrument for Probing Surface Chemical Reactions***, **Peter Amann**,* Scienta Omicron, Germany

Investigating reaction intermediates, oxidation states, solid-liquid interfaces and buried interfaces under near ambient pressure conditions is highly desired in materials science applications. Ambient pressure X-ray photoelectron spectroscopy (APXPS) is a powerful method to investigate the chemical nature of surfaces and interfaces and has undergone a tremendous improvement in the last years. The development of the HiPP analysers allowed to overcome the one bar pressure regime without using pressure separating membranes. [1] [2]

During the past decade, increased attention has been shown to laboratory based APXPS system solutions, which is motivated by the 24/7 access capability and possibility for highly customized sample environments. Drawing on extensive experience in the fields of photoelectron spectroscopy, UHV technology, and system design, Scienta Omicron has designed the HiPPLab as an easy-to-use system that encourages user creativity through flexibility, modularity and an innovate chamber design.[3] It combines a state-of-the-art HiPP analyser with a high flux, variable focus X-ray source. Multiple options complement the HiPPLab offer, including a gas reaction cell, a preparation chamber, laser heating, or options for mass-spectroscopy. Using automated gas-flow controllers, experiments can be conducted in a controlled way. Future upgrade possibilities are given.

The HiPP-3 analyser features a 2D detector allowing for spatial resolved measurements with customer proven results down to 2.8 µm resolution. The swift acceleration mode allows for high electron transmission without applying a sample bias. A sophisticated pre-lens design in which efficient pumping between two close-by apertures is implemented, allows dragging out corrosive gases or moisture, which would otherwise be detrimental to the instrument.

In this presentation, I will give an overview on our APXPS product portfolio focusing on laboratory based solutions and present application examples.

[1] Amann, et al. *Review of Scientific Instruments*, 2019 *90*(10)

[2] Takagi, et al. X-ray photoelectron spectroscopy under real ambient pressure conditions. *Applied Physics Express*, 2017, *10*(7), 8–11.

[3] Scienta Omicron HiPPLab https://scientaomicron.com/en

9:20am **LX+AS+HC+SS-MoM-4 Using Microheaters for Time-Resolved APXPS and Correlated ETEM***, **Ashley Head**,* Brookhaven National Laboratory*; B. Karagoz,* Diamond Light Source, UK*; J. Carpena-Nuñez,* Air Force Research Laboratory*; D. Zakharov,* Brookhaven National Laboratory*; B. Maruyuma,* Air Force Research Laboratory*; D. Stacchiola,* Brookhaven National Laboratory

With a rise in the number of lab-based APXPS systems, these instruments afford an opportunity to continue the development of multimodal and correlated capabilities for more comprehensive information of reactions at surfaces. Here I will discuss the methods of using an ETEM commercial microheater for collecting APXPS data on the same sample under identical conditions. A specialized holder was fabricated to use commercial microheaters on MEMS chips in a lab-based APXPS instrument. The rapid heating of the microheater enables a time-zero for collecting APXPS data with a time resolution of 500 ms. Proof-of-principle measurements following the oxidation and reduction of a Pd film demonstrate correlative experiments with TEM. The specialized holder was fabricated with the possibility of dosing gases locally to the sample surface while confined by a graphene membrane. Using the gas lines, the Pd film was oxidized under a partial pressure of air (~0.4 mbar). Overall, using this microheater in APXPS offers chemical information complementary to structural changes seen in ETEM. The rapid heating enables new opportunities in time-resolution and increased pressure for APXPS experiments.

9:40am **LX+AS+HC+SS-MoM-5 NAP-XPS Instrumentation Came a Long Way - Where Will Applications Lead Us from Here?***, P. Dietrich, F. Mirabella, K. Kunze, O. Schaff,* ***Andreas Thissen,*** SPECS Surface Nano Analysis GmbH, Germany **INVITED**

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 the most important standard surface analytical method in many laboratories for surface and materials characterization.

For the last fifteen years XPS under near ambient pressure conditions (NAP-XPS) has gained significant attention. Although invented as a laboratory method it initially started to grow at synchrotrons. The development of more efficient and sensitive electron analyzers and high-brilliance monochromated laboratory X-ray and UV sources running at pressures of up to 100 mbar finally brought it back to the individual laboratories. The reasons are the availability of individual infrastructure for sample preparation and handling, safety regulations and easier access to measurement time on a daily basis. Nowadays the vast majority of instruments worldwide are laboratory-based.

It opened the method XPS to liquids, solid-liquid interfaces, gas-solid-interfaces, gas-liquid-interfaces and many more. The development of instrumentation followed the important applications and besides the "active" components, mainly excitation sources and electron analyzers, a lot of developments have been done in the fields of sample environments, sample handling, system setup and automation and combination with other techniques and even in quantification of data. There are only a few applications left where experiments at synchrotron based beamlines and end stations offer the only solution.

The market driving applications nowadays are catalysis, electrochemistry, behaviour of liquid phases, biological samples and surface chemistry. Along these applications this presentation will show the existing instrumentation, discuss its limits and the perspective for near future developments to further increase the user base of laboratory based NAP-XPS systems to turn it into an integral part of the large routine analysis community.

10:40am **LX+AS+HC+SS-MoM-8 Evolution of Metal-Organic Frameworks in the Presence of a Plasma by AP-XPS and IRRAS***,* ***J. Anibal Boscoboinik,*** Brookhaven National Laboratory and State University of New York at Stony Brook*; M. Ahmad,* Stony Brook University/Brookhaven National Laboratory*; M. Dorneles de Mello,* Brookhaven National Laboratory*; D. Lee,* Johns Hopkins University*; P. Dimitrakellis,* University of Delaware*; Y. Miao,* Johns Hopkins University*; W. Zheng,* University of Delaware*; D. Nykypanchuk,* Brookhaven National Laboratory*; D. Vlachos,* University of Delaware*; M. Tsapatsis,* Johns Hopkins University **INVITED**

Zeolitic imidazolate frameworks (ZIF), a class of metal-organic frameworks, are promising materials for various applications, including the separation and trapping of molecules and catalysis. Recent work has shown that exposure to plasma can result in the functionalization of the framework for tailored applications. This talk will report in-situ plasma studies of ZIF-8 as a model system. We will study the framework's evolution in the presence of N_2, O_2, and H_2 plasmas by combining lab-based ambient pressure XPS and infrared reflection absorption spectroscopy.

11:20am **LX+AS+HC+SS-MoM-10 Surface Degradation and Passivation in Perovskite Solar Cells***,* ***Wendy Flavell,*** The University of Manchester, UK **INVITED**

There is an urgent requirement to make better use of the 120,000 TW of power provided by the Sun, by using it to generate power, or by using its energy directly to make useful chemical feedstocks. Around the world, there is an explosion of research activity in new systems for harvesting solar energy, including solar cells based organometal halide perovskites. Issues of key importance are the interfacial energy level line-up of the cell components, and the influence of the surface properties of these materials on charge separation in the devices. Indeed, the deployment of perovskites in solar cells is currently limited by their high reactivity and rate of surface oxidation. Thus, a key problem is to develop an understanding of the interface chemistry of solar heterojunctions in order to develop passivation strategies. I show how a combination of techniques including near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) and hard X-ray photoelectron spectroscopy (HAXPES) may be used to investigate surface ageing and the surface degradation reactions[1-7], chemical composition as a function of depth[4,5], and to develop passivation strategies for perovskite solar cell heterojunctions[2,3,5-7].

References

1. J C-R Ke, A S Walton, A G Thomas, D J Lewis, *et al.*, *Chem Commun* **53**, 5231 (2017).
2. J C-R Ke, D J Lewis, A S Walton, B F Spencer, *et al.*, *J Mater Chem A*, **6**, 11205 (2018).
3. C-R Ke, D J Lewis, A S Walton, Q Chen, *et al., ACS Applied Energy Materials* **2**, 6012 (2019).
4. B F Spencer, S Maniyarasu, B P Reed, D J H Cant *et al.*, *Applied Surface Science* **541**, 148635 (2021).
5. S Maniyarasu, J C-R Ke, B F Spencer, A S Walton *et al.,ACS Applied Energy Materials* **13**, 43573 (2021).
6. S Maniyarasu, B F Spencer, H Mo, A S Walton *et al.*, *J Mater Chem A*, **10**, 18206 (2022).
7. D Zhao, T A Flavell, F Aljuaid, S Edmondson*et al., ACS Applied Materials and Interfaces,* submitted.

Chemical Analysis and Imaging of Interfaces Focus Topic
Room A105 - Session CA+AS+LS+NS+SS+VT-MoA

Environmental and Energy Interfaces

Moderators: Musahid Ahmed, LBNL, **Xiao-Ying Yu**, Oak Ridge National Laboratory, USA

1:40pm **CA+AS+LS+NS+SS+VT-MoA-1 In situ Spectroscopies of Interfacial Reactions and Processes in Batteries***, **Feng Wang**,* Argonne National Laboratory **INVITED**

The performance and lifetime of batteries, whether they are traditional lithium-ion, solid-state, or other types, strongly depend on the effectiveness and stability of electrochemical interfaces within the devices. To design battery materials and interfaces with desired functionality, it is crucial to have a mechanistic understanding of the interfacial reactions and processes occurring during battery operation. This necessitates developing advanced techniques capable of characterizing local structures and capturing *non-equilibrium* dynamics at electrochemical interfaces, with the relevant spatial, time resolution and chemical sensitivity, both to light elements (H, Li, O) and heavy ones. Herein, we present the development and application of *in situ* spectroscopies specialized for probing interfacial reaction and processes in lithium-ion and solid-state batteries. With specific examples from our recent studies, we will show how to correlate the structure and function of electrochemical interfaces through *in situ* spectroscopy characterization, thereby gaining insights into the design and processing of battery materials, electrolytes and other components. Towards the end of this talk, we will discuss emerging opportunities in data-driven experimentation, analysis, and modeling for closed-loop battery development to accelerate the transition from lab discovery to commercial deployment.

2:20pm **CA+AS+LS+NS+SS+VT-MoA-3 Novel Strategies for the Characterization of the Next-Generation Energy Storage Materials by ToF-SIMS: From an in-Situ Exploration to an Operando Measurement***, **Tanguy Terlier**, Q. Ai, S. Sidhik, A. Mohite, J. Lou,* Rice University **INVITED**

Recently, advances in instrumentation and sample preparation have permitted a rapid development for characterizing a wide range of applications such as next-generation energy storage materials. Developing new materials is one of the most crucial topics for emerging technologies. However, the complexity of these materials in their structures makes them particularly challenging for numerous characterization and analytical techniques. Exploring chemical composition and the potential chemical reactions such as degradation, diffusion, or doping is crucial to understand advanced materials and to transfer the new technologies to the industry. Among the most suitable characterization tool, time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a very sensitive surface analytical technique providing detailed elemental and molecular information about the surface, thin layers, interfaces, and full three-dimensional analysis of the samples.

Thanks to the advances in ToF-SIMS characterization, understanding of the chemical composition and the different components in the complex structures, permit a deeper exploration and a better knowledge in the next-generation energy storage materials such as batteries, perovskites, and 2D materials.

Firstly, we will focus on the characterization of batteries. Initially, we will discuss the sample preparation and our specific setup for transferring the specimens from the inert atmosphere in the glovebox to the ultra-high vacuum chamber of our instrument. We will illustrate the possibility to study the reversibility of the chemical composition between pristine, charged, and discharged batteries using surface mass spectrometry by ToF-SIMS in operando conditions. Then we will compare three methods of cross-sectioning used to identify the interfacial species in a composite cathode.

Secondly, we will show a study of an in-depth distribution of the 3D/2D heterostructures for perovskite solar cells where we have been able to identify individually the 3D and 2D heterostructures along with the depth of the film. Then, we will illustrate the characterization of interdiffusion in quasi-2D perovskite light-emitting diodes as a function of the organic ligand layer inserted into the perovskite crystals.

Finally, we will demonstrate how the retrospective analysis using ToF-SIMS can be very powerful and useful for exploring any single feature in 2D materials. Typically, ToF-SIMS acquisition is recording a full mass range spectrum per pixel (or voxel), which permits to isolate and to decorrelate specific regions of interest for resolving interfaces, diffusion, and doping in thin 2D structures. We will present how to treat a 3D volume image of a multilayer perovskite device for extracting useful information.

3:00pm **CA+AS+LS+NS+SS+VT-MoA-5 Advanced In-Situ and Ex-Situ S/TEM Probing of Interfacial Process in Rechargeable Batteries***, **Chongmin Wang**,* Pacific Northwest National Laboratory

In-situ diagnosis appears to be one of the essential methods for gaining insights as how an electrode material failure, therefore feeding back for designing and creating new materials with enhanced battery performances. In this presentation, I will highlight recent progress on ex-situ, in-situ and operando S/TEM for probing into the structural and chemical evolution of interfacial process in energy storage materials. Both ex-situ and In-situ high resolution imaging enables direct observation of structural evolution, phase transformation and their correlation with mass, charge and electron transport, providing insights as how active materials failure during the cyclic charging and discharging of a battery. In perspective, challenges and possible direction for further development of the in-situ S/TEM imaging and spectroscopic methods for energy storage materials and other field will also be discussed. Most importantly, integration of different analytical tools appear to be the key for capturing complementary information.

3:20pm **CA+AS+LS+NS+SS+VT-MoA-6 Investigating sp^2 and sp^3 Carbon Ratios by XPS: A Study of the D-Parameter and a New Second Plasmon Loss (2PL) Parameter***, **Alvaro Lizarbe**, G. Major, B. Clark,* Brigham Young University*; D. Morgan,* Cardiff University, UK*; M. Linford,* Brigham Young University

The D-parameter provides a useful estimate of the ratio of the sp^2 and sp^3 carbon in a sample. It is the energy difference between the maximum and minimum of the derivative of the C KLL Auger peak. The D-parameter can be an important analytical resource for diamond samples, as the quality of diamond depends on the sp^3 to sp^2 carbon ratio and any lattice impurities. For example, the highly sought after type 2a diamonds, which are colorless and free from impurities, consist almost entirely of sp^3 carbon. According to the universal curve for XPS, electrons with different kinetic energies have different mean free paths. Thus, electrons with different kinetic energies sample materials at different depths. In the case of carbon, the KLL Auger peak comes shallower in a material compared to the C 1s signal, which is a result of electrons with much higher kinetic energies. That is, a limitation of the D-parameter is that it is based on the C KLL Auger peak, found at around 1220 eV, while it is often related to the C 1s peak located at approximately 284.8 eV. Thus, the D-parameter is much more sensitive to adventitious carbon contamination. In an effort to derive a parameter that will be more representative of the amounts of sp^2 and sp^3 carbon in a material, we have examined the plasmon loss peaks of the zero-loss C 1s peak of direct current chemical vapor deposition (DC-CVD) diamonds, carbon nanotubes, and graphitic materials such as HOPG. By analyzing the second plasmon loss signal of the C 1s narrow scan, we obtain a new parameter for analyzing carbonaceous materials: the 2PL parameter. The 2PL parameter is the difference in energy between the second plasmon loss signal and the C 1s peak. We compare the traditional D-parameter with the 2PL parameter for various materials. They correlate quite well. We have also investigated various mathematical methods of deriving the 2PL parameter, including via a weighted average of the second plasmon loss and C 1s signals. Ultimately, because the 2PL parameter involves signals that are closer to the C 1s photoemission binding energy, we believe it may be more representative of the full chemistry of carbonaceous materials.

4:00pm **CA+AS+LS+NS+SS+VT-MoA-8 Solid-Liquid Interfaces for Energy-efficient Chemical Separation of Critical Minerals and CO_2 Conversion***, **Manh-Thuong Nguyen**, V. Prabhakaran, D. Heldebrant, G. Johnson,* Pacific Northwest National Laboratory **INVITED**

Chemical separations consume around 15% of the energy used by industry today. It is thus critical to develop energy- and material-efficient approaches for large-scale separations. In the first part of this presentation, I will illustrate how we employ modified 2-dimensional materials and solvents to separate critical minerals including rare earth elements. Polar functional groups present at the interface of graphene oxide laminate membranes are demonstrated to improve the selectivity of metal cations separated by both adsorption and sieving. Hydrophobic ionic liquid molecules including 1-ethyl-3-methylimidazolium chloride, when used as a minor solvent component, are shown to increase the energy efficiency of the desolvation of aqueous lanthanide cations in electrochemical separations. In the second part, I will present studies exploring the use of functionalized hexagonal boron nitride (h-BN) membranes to separate CO_2

from multicomponent gas mixtures. Strategies for improving CO_2 separation selectivity and efficiency, such as chemical functionalization and engineering the dimensions of interlayer transport channels, will be discussed. Finally, I will present studies on the electrochemical conversion of CO_2 into value added chemical feedstocks such as methanol on membrane-supported catalysts. Insights into the effects of local structure modification and confinement on catalytic processes will be presented.

4:40pm **CA+AS+LS+NS+SS+VT-MoA-10 Buried Interfaces of Ir Photodetector Devices Analyzed with Lab-Based Xps/Haxpes***, **Roman Charvier**, M. Juhel,* STMicroelectronics, France*; O. Renault,* Univ. Grenoble-Alpes, CEA, Leti, France*; A. Valery, D. Guiheux, L. Mohgouk Zouknak,* STMicroelectronics, France*; B. Domenichini,* ICB UMR 6303 CNRS-Université de Bourgogne, France

The development of new IR photodetectors should respond to challenges in order to reach best performances. A major objective is to understand critical interfaces that play an important role in the final device properties. This work addresses to chemical analysis of molybdenum oxide (MoO_{3-x}) used as hole transport material which is deposited between a photosensitive material and top electrode often made of indium-tin oxide (ITO). Such critical interfaces are typically located under 20 to 50 nm under the surface.

In the case of MoO_{3-x}, the stoichiometry is generally controlled by X-ray photoelectron spectroscopy (XPS) which is well-known to obtain chemical data close to the material surface (analysis depth < 10 nm). Two methods can be used to analyse deeper buried layers: (i) the use of hard X-rays to perform Hard X-ray PhotoElectron Spectroscopy (HaXPES) and thus generate photoelectrons having a kinetic energy able to go through several tens of nm; (ii) the etching of the surface by means of an Ar^+ beam (having an energy from 0.5 to 3 keV) in order to remove the superficial layers giving access to the underlying layers. In the former case, the analyzed thickness remains far below 100 nm while in the latter case, the chemistry of the surface atoms are often modified by argon ion beam. It is then necessary to mix the two approaches to allow the chemical analysis of buried interfaces. This analysis way is used here to characterize the stoichiometry of MoO_{3-x} thin films buried under 50 nm of ITO using chromium Kα hard-X-ray from lab-based HaXPES.

5:00pm **CA+AS+LS+NS+SS+VT-MoA-11 Detection and Discrimination of Aquatic Toxins Targeting Voltage Gated Sodium Channels Using Static ToF-SIMS Imaging***, **Jiyoung Son**, K. Engbrecht, J. Mobberley,* PNNL

Neurotoxins from aquatic microorganisms, such as cyanobacteria and algae, have been a public health concern due to their harmful impacts on the nervous systems of animals, including humans. A subset of these neurotoxins, including saxitoxin and brevetoxin, bind to and alter the function of voltage-gated sodium channels, which are essential to generating the cell membrane action potential. Existing detection and categorization methods, such as PCR and antibody-based enzyme-linked immunosorbent assays, are too specific and they require live animals like the mouse bioassay. They also require time-consuming and expensive sample preparation for analysis using LC-MS/MS and HPLC. In this project, we developed a method to detect the activity of the aquatic sodium channel neurotoxins, brevetoxin and saxitoxin, using a cell-based process. We specifically examined the impact of these two neurotoxins on HEK-293 cells, a robust cell line that has been transfected with a voltage-gated sodium channel gene, SCN1A, in order to better study neurotoxins. We cultured a layer of cells onto disinfected silicon chips, exposed the cells to neurotoxins, performed chemical fixation, and then air-dried the chips. We also prepared mock exposed samples where the cells on the silicon chips were not exposed to neurotoxins, but just the solutions each neurotoxin was resuspended in, either a 3mM HCl solution (mock saxitoxin) or a 50:50 ACN: water solution (mock brevetoxin). Control samples, which just exposed cells to cell culture media only, gave us a baseline reference. Dried samples were analyzed with mass spectral imaging using time-of-flight secondary ion mass spectrometry (ToF-SIMS). After collecting a series of spectral data, we utilized an in-house MATLAB tool to run principal component analysis (PCA) as previously described (Yu et al., 2020). Our initial statistical analysis of SIMS spectral data using PCA shows a noticeable difference in peak trends between neurotoxin and mock-exposed cells as well as neurotoxin-exposed and control cells. Our approach utilizes chemical imaging to develop a threat-agnostic model system for detecting and classifying neurotoxin activity. The technology and protocols developed from this work could transition to other rapid cellular assays for pathogenic and chemical threats.

Reference

Yu, J., Zhou, Y., Engelhard, M. *et al.In situ* molecular imaging of adsorbed protein films in water indicating hydrophobicity and hydrophilicity. *Sci Rep***10**, 3695 (2020). https://doi.org/10.1038/s41598-020-60428-1

Laboratory-Based Ambient-Pressure X-ray Photoelectron Spectroscopy Focus Topic
Room B116 - Session LX+AS+BI+HC+SS+TH-MoA

Laboratory-Based AP-XPS:Surface Chemistry and Biological/Pharmaceutical Interfaces

Moderators: Gregory Herman, Argonne National Laboratory, **Ashley Head**, Brookhaven National Laboratory

1:40pm **LX+AS+BI+HC+SS+TH-MoA-1 The Role of Co-Adsorbed Water in Decomposition of Oxygenates***, H. Nguyen, K. Chuckwu, **Líney Árnadóttir**,* Oregon State University **INVITED**

The decomposition of oxygenates in the presence of water finds various applications in chemical processes, such as biomass conversion. The presence of co-adsorbates and solvents affects both the reaction rate and selectivity. In this study, we used NAP-XPS and DFT to investigate the decomposition of acetic acid on Pd(111) as a model system for the decomposition of small oxygenates in the absence and presence of water. The decomposition of acetic acid occurs through two main reaction pathways, decarboxylation, and decarbonylation, forming CO_2 or CO, respectively. Our DFT calculations indicate that the two pathways have similar barriers without water. However, in the presence of water, the decarboxylation path becomes. Similarly, our AP-XPS experiments show an increase in the CO_2/CO ratio as well as a decrease in the CO/acetate-acetic acid and acetic acid/acetate ratios when water is present. The shift in selectivity is not due to a single reaction step, but rather the decreasing barrier in general for OH scissoring and the increasing barrier for C-O scissoring. This shift favors the formation of CO_2, as demonstrated by our microkinetic model.

2:20pm **LX+AS+BI+HC+SS+TH-MoA-3 Integrating First-principles Modeling and AP-XPS for Understanding Evolving Complex Surface Oxides in Materials for Hydrogen Production and Storage***, B. Wood, **Tuan Anh Pham**,* Lawrence Livermore Laboratory **INVITED**

Chemical processes occurring at solid-gas, solid-liquid, and solid-solid interfaces critically determine the performance and durability of hydrogen production and storage technologies. While directly probing behavior of these interfaces under actual operating conditions remains challenging, modern surface science approaches such as ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) can provide insight into the evolution of surface chemistry in approximate environments. However, interpretation of these spectra can be complicated: standards for complex surface chemical moieties are often unavailable, and bulk standards can be unreliable. First-principles computations are emerging as an important companion approach, offering the ability to directly compute spectroscopic fingerprints. This has the advantage of aiding interpretation of the experiments, while simultaneously using the experiment-theory comparison to inform construction of more accurate interface models. In this talk, I will show how computation has been combined with laboratory-based AP-XPS measurements to understand the evolving chemistry of complex native surface oxides. Two examples will be drawn from activities within the U.S. Department of Energy HydroGEN and HyMARC consortia, which focus on renewable hydrogen production and materials-based hydrogen storage, respectively. First, I will discuss the application to surface oxidation of III-V semiconductors for photoelectrochemical hydrogen production, which demonstrates transitions between kinetically and thermodynamically controlled oxidation regimes with implications for device performance. Second, I will also show how the same approach has been applied to understand the rate-determining role of surface oxides in the dehydrogenation performance of $NaAlH_4$ for solid-state hydrogen storage.

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

3:00pm **LX+AS+BI+HC+SS+TH-MoA-5 Particle Encapsulation on Reducible Oxides Under Near-Ambient Pressures***, F. Kraushofer, M. Krinninger, P. Petzoldt, M. Eder, S. Kaiser, J. Planksy, T. Kratky, S. Günther, M. Tschurl, U. Heiz, F. Esch, **Barbara A. J. Lechner,*** TUM, Germany **INVITED**

Catalysts on reducible oxide supports often change their activity significantly at elevated temperatures due to the strong metal-support interaction (SMSI), which induces the formation of an encapsulation layer around the noble metal particles. However, the impact of oxidizing and reducing treatments at elevated pressures on this encapsulation layer remains controversial, partly due to the 'pressure gap' between surface science studies and applied catalysis.

In the present work, we employ near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) and scanning tunneling microscopy (NAP-STM) to study the effect of reducing and oxidizing atmospheres on the SMSI-state of well-defined oxide-supported Pt catalysts at pressures from UHV up to 1 mbar. On a $TiO_2(110)$ support, we can either selectively oxidize the support or both the support and the Pt particles by tuning the O_2 pressure.[1] We find that the growth of the encapsulating oxide overlayer is inhibited when Pt is in an oxidic state. Our experiments show that the Pt particles remain embedded in the support once encapsulation has occurred. On $Fe_3O_4(001)$, the encapsulation stabilizes small Pt clusters against sintering.[2] Moreover, the cluster size and thus footprint lead to a change in diffusivity and can therefore be used to tune the sintering mechanism. Very small clusters of up to 10 atoms even still diffuse intact after encapsulation.

[1] P. Petzoldt, P., M. Eder, S. Mackewicz, M. Blum, T. Kratky, S. Günther, M. Tschurl, U. Heiz, B.A.J. Lechner, Tuning Strong Metal–Support Interaction Kinetics on Pt-Loaded TiO_2 (110) by Choosing the Pressure: A Combined Ultrahigh Vacuum/Near-Ambient Pressure XPS Study, *J. Phys. Chem. C*126, 16127-16139 (2022).

[2] S. Kaiser, J. Plansky, M. Krinninger, A. Shavorskiy, S. Zhu, U. Heiz, F. Esch, B.A.J. Lechner, Does Cluster Encapsulation Inhibit Sintering? Stabilization of Size-Selected Pt Clusters on $Fe_3O_4(001)$ by SMSI, *ACS Catalysis* 13, 6203-6213 (2023).

4:00pm **LX+AS+BI+HC+SS+TH-MoA-8 Applications of NAP XPS in Pharmaceutical Manufacturing: Surface Analysis, Hydrogen Bonds, and Solute-Solvent Interactions***, **Sven Schroeder,*** University of Leeds, UK **INVITED**

The availability of laboratory-based NAP XPS creates novel interface research opportunities for scientific disciplines and technology areas that deal with materials incompatible with traditional ultra-high vacuum XPS. This is, for example, the case for many organic and/or pharmaceutical materials and formulations, whose characterization by XPS has hitherto been restricted by their vapour pressures. NAP XPS permits for the first time systematic and detailed analysis of the light element photoemission lines (expecially C/N/O 1s) in these materials. In conjunction with elemental analysis by survey XP spectra they provide quantitative information on composition and speciation both in the bulk and at the surfaces of pure organic solids, in their formulations with other components and in solutions. Especially of interest are studies of the solid/liquid interface with water, which is of high relevance for understanding and controlling drug release profiles from tablets. To illustrate these points I will present various examples of research on pharmaceutical materials. Moreover, near-ambient pressure core level spectroscopy turns out to be an extremely powerful probe for the structure and dynamics of hydrogen bonding and proton transfer in materials, both in the solid state and in solutions. NAP XPS measurements provide unique insight into proton dynamics in noncrystalline solids and liquids, where traditional characterisation by crystallography and nuclear magnetic resonance fails or provides ambiguous information on proton locations.

4:40pm **LX+AS+BI+HC+SS+TH-MoA-10 The Change of DNA and Protein Radiation Damage Upon Hydration: In-Situ Observations by Near-Ambient-Pressure XPS***, **Marc Benjamin Hahn,*** Bundesanstalt für Materialforschung und -prüfung (BAM), Germany **INVITED**

X-ray photoelectron-spectroscopy (XPS) allows simultaneous irradiation and damage monitoring. Although water radiolysis is essential for radiation damage, all previous XPS studies were performed in vacuum. [1] Here we present near-ambient-pressure XPS experiments to directly measure DNA damage under water atmosphere. They permit in-situ monitoring of the effects of radicals on fully hydrated double-stranded DNA. Our results allow us to distinguish direct damage, by photons and secondary low-energy electrons (LEE), from damage by hydroxyl radicals or hydration induced modifications of damage pathways. The exposure of dry DNA to x-rays leads to strand-breaks at the sugar-phosphate backbone, while deoxyribose and nucleobases are less affected. In contrast, a strong increase of DNA damage is observed in water, where OH-radicals are produced. In consequence, base damage and base release become predominant, even though the number of strand-breaks increases further. Furthermore, first data about the degradation of single-stranded DNA binding-proteins (G5P / GV5 and hmtSSB) under vacuum and NAP-XPS conditions are presented.

[1] Hahn, M.B., Dietrich, P.M. & Radnik, J. In situ monitoring of the influence of water on DNA radiation damage by near-ambient pressure X-ray photoelectron spectroscopy. Commun Chem 4, 50, 1-8 (2021). https://doi.org/10.1038/s42004-021-00487-1

Surface Science Division
Room D136 - Session SS+AS+TF-MoA

Mechanisms at Surfaces and Interfaces

Moderators: Florencia C. Calaza, Instituto de Desarrollo Tecnológico para la Industria Química, **Jun Nakamura**, UEC Tokyo

1:40pm **SS+AS+TF-MoA-1 Spin- and Alignment-Controlled O_2 Chemisorption and Catalytic CO Oxidation on Stepped Pt and Pt/Co Alloy Surfaces***, **Mitsunori Kurahashi,*** National Institutes for Materials Science, Japan **INVITED**

O_2 chemisorption and catalytic oxidation on Pt and its alloy surfaces have been studied intensively due to the relevance to important processes such as car exhaust gas purification and oxygen reduction reaction (ORR) in fuel cell. Since O_2 is a linear diatomic molecule with an electron spin, the alignment of the O_2 axis relative to the surface local structure is a key to understand the elementary processes of O_2 chemisorption. If the surface is magnetic, the spin correlation between O_2 and the surface also plays an important role. A single spin-rotational state-selected [(J,M)=(2,2)] O_2 beam allows us to investigate the effects of molecular alignment and spin on O_2/surface interactions [1].

In this talk, I will firstly present the alignment-controlled O_2 chemisorption and CO oxidation on curved Pt(111). The use of a curved crystal surface and a local probe allows us to monitor the step-density dependence in surface properties or reactivity[2,3]. In this study, by scanning the aligned O_2 beam with a dimension of 0.2mmW x 2mm across a curved Pt(111) surface, the step-density and structure dependence in alignment-resolved O_2 chemisorption probability and CO oxidation rate were measured. The results indicate that step affects the reactivity of the neighboring terraces, and that the low temperature CO oxidation rate at step site is much lower than at (111) terrace.

Secondly, I will present the spin-dependent catalytic CO oxidation on Pt/Co/Pt(111). Pt/Co alloy has attracted much attention since it shows a higher ORR activity than pure Pt [4]. The higher reactivity has been attributed to the charge transfer from the subsurface Co to the surface Pt layer while how the spin of the subsurface Co affects the reactivity of the surface Pt remains unclear. Spin-resolved O_2 chemisorption and CO oxidation experiments on a perpendicularly-magnetized Pt/Co(2ML)/Pt(111) film indicate that the O_2 chemisorption probability and the catalytic oxidation rate depend strongly on the spin orientation between O_2 and the Pt surface. The magnitude of the spin orientation dependence was larger than that observed for O_2/Ni [1,5]. An SPMDS measurement and DFT calculation show that the surface Pt layer is spin-polarized at around E_F. The present experiments indicate that the catalytic activity of Pt is strongly affected by the magnetism of neighboring atoms.

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2:20pm **SS+AS+TF-MoA-3 Atomic-Scale Insights Into the Sintering Resistance and Oxidation of Single-Atom Alloys***, **Audrey Dannar**[1],* Tufts University*; J. Finzel,* University of California, Santa Barbara*; V. Cinar, E. Sykes,* Tufts University

Copper-based catalysts are used in a wide range of heterogeneous catalytic processes that can take place in oxidizing environments, where Cu is known to readily oxidize to form CuOx, and reducing environments, where Cu is known to deactivate via sintering. Single-atom alloys (SAAs) are a new type

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

of catalyst in which isolated atoms of dilute reactive dopants such as Pt and Rh are present in more inert host metals such as Cu. Despite their great promise for hydrogenation and dehydrogenation reactions, there exists limited understanding of these materials under oxidizing conditions. Similarly, SAAs have shown exceptional long-term stability with anecdotal reports of sintering resistance in industrial conditions that are not presently fundamentally understood. This work aims to develop atomic-scale structure-function relationships for Cu-based catalysts that span oxidizing and reducing conditions and understand how single dopant atoms stabilize the undercoordinated Cu atoms responsible for sintering and involved in CuOx formation upon O2 exposure.

First, we used a specialized method for measuring the surface diffusion of metal atoms that leads to sintering with scanning tunneling microscopy (STM) experiments which reveals that single Pt atoms in a Cu(110) surface significantly reduce the rate of Cu atom detachment from undercoordinated surface sites. Thus, the origin of sintering resistance exhibited by SAA is hypothesized to be due to dopant atom stabilization of undercoordinated Cu atoms at the step edge. This is validated by DFT and paired with collaborator work that shows PtCu/SiO2 dilute alloy catalysts are significantly more stable than monometallic Cu/SiO2 in methanol synthesis experiments via EXAFS and TEM.

Next we used STM experiments to elucidate atomic-scale details of the oxidation processes of both PtCu(111) and RhCu(111) SAAs. STM images reveal that on Cu(111), oxidation occurs below Cu step edges, consistent with literature reports. Interestingly, for the RhCu(111) SAA, oxidation occurs both below the step edges and also above, where the Rh atoms are located, but this is not the case for the Pt brim on PtCu(111). For both Rh and Pt SAAs the oxidation below the step edge is reduced compared to Cu, which we hypothesize is due to the stabilization of Cu step edge atoms, which are required to restructure during CuOx formation below the step. The reduced rates of sintering and oxidation of PtCu SAAs compared to Cu originate from Cu step edge atoms being kinetically stabilized by dilute dopants. Together, these results begin to shed light on the role of single dopant atoms in the mechanisms Cu nanoparticle sintering and Cu oxidation.

2:40pm **SS+AS+TF-MoA-4 Visualization of the Local Dipole Moment at the Si(111)-(2x2) Surface Using DFT Calculations***, **Akira Sumiyoshi**, J. Nakamura,* The University of Electro-Communications (UEC Tokyo), Japan

Understanding the polarization state of a sample is essential in the development of devices and functional materials. Recently, the spatial distribution of the surface polarization has been observed using new microscopy techniques, such as SNDM[1-3]. However, there have yet to be any reports regarding the theoretical simulation of surface polarization. Here, we focused on the dipole moment (DM), an essential aspect of polarization, and developed a method to visualize the distribution of surface DM using theoretical calculations. In this study, we report on the surface DM distribution of Si(111)-(2x2) with the characteristic motif of the Si(111)-(7x7) DAS structure. Furthermore, we confirmed that the surface dipole distribution can be explained consistently with the surface stabilization mechanism.

We defined and calculated the DM using the following formula;

$\mu_{(x,y,z)} = \int \rho_{(x,y,z')} * (z'-z_0)\, dz'$

Here, μ is the DM, $\rho_{(x,y,z')}$ is the total charge density, and z_0 is the origin in the vertical direction. In order to eliminate the effect of the backside surface of the Si(111) slab, we adopted the midpoint of the deepest bulk layer of the slab as the origin and integrated the above formula from z_0 to the vacuum position z sufficiently far from the topmost surface. The total charge density was calculated using DFT-based first-principles calculations.

Upon optimizing the structure, the restatom was lifted compared to the original bulk position, suggesting the larger orbital electronegativity[4] of the surface orbital of the restatom[5]. This change in orbital electronegativity leads to an electron transfer from the adatom to the restatom, resulting in no surface dangling bond. We calculated the electron localization function (ELF) map and the band diagram to confirm the surface electron transfer. We confirmed the presence of the electron pair on the restatom from ELF. It was revealed that the Si(111)-(2x2) surface has a finite energy gap. As a result, it was clearly shown that the electron transfer occurs from the adatom to the restatom, emptying the dangling bond at the adatom and forming a lone pair at the restatom.

Furthermore, we simulated the surface DM distribution. As a result, an upward DM was observed at the adatom position, which is explained by the depletion of electrons just above the adatom due to the electron transfer at the surface.

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3:00pm **SS+AS+TF-MoA-5 Mechanism Study of a Chemisorbed O_2 Molecule on Ag(110) Induced by High-Order Overtone Excitation Using STM***, **Minhui Lee**, E. Kazuma,* The University of Tokyo, Japan*; C. Zhang,* Tongji University, China*; M. Trenary,* University of Illinois at Chicago*; J. Takeya,* The University of Tokyo, Japan*; J. Jung,* University of Ulsan, Republic of Korea*; Y. Kim,* The University of Tokyo, Japan

The dissociation pathway of chemisorbed O_2 on Ag(110) was elucidated by single-molecule microscopic and spectroscopic studies using a scanning tunneling microscope (STM). The dissociation reaction was found to be predominantly triggered by inelastically tunneled holes from the STM tip due to the significantly distributed density of states below the Fermi level of the substrate. A combination of action spectroscopy with the STM and density functional theory calculations revealed that the O_2 dissociation reaction is caused by direct ladder-climbing excitation of the high-order overtones of the O-O stretching mode arising from anharmonicity enhanced by molecule-surface interactions.

3:20pm **SS+AS+TF-MoA-6 Characterization of Oxygen Evolution from Rh(111)***, **Maxwell Gillum**, E. Jamka, F. Lewis, D. Killelea,* Loyola University Chicago

Due to the importance of oxide surfaces in heterogeneously catalyzed reactions, it is critical to gain a fundamental understanding of the reactivity and behavior of oxygen on these transition metal surfaces. In previous studies we have been able to establish that the reactivity and thermodynamic stability of oxygen on Rh(111) relies in part on the concentration of oxygen present in the subsurface. However, more research needs to be conducted in order to gain a better understanding of the relationship between surface reactivity and subsurface concentration. In addition to the techniques used in our previous studies, namely temperature programmed desorption (TPD) and scanning tunneling microscopy (STM), the experiments herein will include simultaneous infrared (IR)/TPD techniques to gain more information on these critical interactions.

4:00pm **SS+AS+TF-MoA-8 Spin-Polarized VLEED from Au(111): Surface Sensitivity of the Scattering Process***, **Christoph Angrick**, A. Reimann,* University of Münster, Germany*; J. Braun,* Ludwig-Maximilians-University of Munich, Germany*; M. Donath,* University of Münster, Germany

Low-energy electron diffraction from Au(111) shows the well-known threefold symmetry of the diffracted electron beams despite the sixfold symmetry of the surface layer. This is due to the influence of the second and deeper layers and the probing depth of the electrons. In this work, we investigated Au(111) with spin-polarized very-low-energy electron diffraction (VLEED) [1,2,3] experimentally and theoretically. We monitor the reflected specular beam at a fixed polar angle of incidence of Θ=45° while the azimuthal orientation of the crystal is varied. This puts the surface sensitivity of the VLEED scattering process to a test.

Our results show that the electron reflection and the spin-orbit-induced reflection asymmetry along ΓM and ΓM' are equivalent. The observed sixfold symmetry suggests a sensitivity to one atomic layer only. At azimuth angles deviating from the high-symmetry directions ΓM and ΓM', however, the VLEED signal from Au(111) shows a threefold symmetry. To reveal the origin of this effect, we varied the parameters in the calculation. The results indicate a non-negligible influence of the second atomic layer in the VLEED scattering process.

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4:20pm **SS+AS+TF-MoA-9 Unravelling the Chemisorption Mechanism of Epoxy-Amine Coatings on Zr-Based Converted Galvanized Steel by Combined Static XPS/ToF-SIMS Approach***, **Vanina Cristaudo**, K. Baert, P. Laha,* Research Group Electrochemical and Surface Engineering (SURF), Vrije Universiteit Brussel, Belgium*; M. Lim, L. Steely, D. Clingerman, E. Brown-Tseng,* Coatings Innovation Center, PPG*; H. Terryn, T. Hauffman,* Research Group Electrochemical and Surface Engineering (SURF), Vrije Universiteit Brussel, Belgium

In the automotive industry, the corrosion protection of hot-dip galvanized (HDG) steel is of primary importance. To this purpose, a Zr oxide-based conversion pre-treatment of the metal surface for passivation and improved adhesion [1], in combination with the application of a polymeric primer coating is often performed. Usually, organic and inorganic additives are used in the acidic conversion bath for a large variety of purposes. For instance, Cu(II) salts are employed to accelerate the deposition of zirconium oxide [1]. Recently, the heterogeneity and multi-metal nature of the resulting surface has been demonstrated in our laboratory [2]. Now, it is of pivotal importance to study the efficiency and durability of such hybrid (hydr)oxide-polymer systems, which depend on the formation and degradation of the chemical bonds at the buried interface.

This work aims at the elucidation of the interfacial interactions established between an epoxy-amine coating and HDG steel [3]. The influences of the Zr-based conversion treatment of the substrate and the use of Cu(II) additive on interfacial bonding will be studied [3]. To this purpose, an amine-functionalized molecule – diethylenetriamine (DETA), a common curing agent – will be adsorbed and used as an indicator of the acid-base properties of the metal oxide surface. The complex multi-metal oxide surface of the Cu-modified Zr-based converted substrate will be decomposed in derivative (simpler) systems, such as pure Zn, Zr, and Cu. The resulting DETA-adsorbed model and multi-metal surfaces will be investigated by X-ray photo-electron spectroscopy (XPS), and by examination of the N 1s peak, the interfacial bond densities will be determined. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) will be performed to discriminate between the different metal oxide contributions present on the substrate surface. Preferential adsorption of the DETA molecule on the zinc atoms is found on converted substrates. SIMS also points out the interfacial bonding with the Cu cationic sites when the copper additive is used, highlighting the extreme usefulness of this analytical technique in the assessment of interfacial interactions of "diluted" adsorption sites.

References

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4:40pm **SS+AS+TF-MoA-10 Fermi Surface Emergence and Valence Band Maximum Formation During Li$_x$CoO$_2$ Insulator-to-Metal Transition***, **Elena Salagre**,* Dpto Física Materia Condensada, Universidad Autónoma de Madrid, Spain*; P. Segovia,* Dpto Física Materia Condensada, Universidad Autónoma de Madrid. IFIMAC (Condensed Matter Physics Center), Spain*; M. González-Barrio,* Dpto Física de Materiales, Universidad Complutense de Madrid, Spain*; J. Pearson, I. Takeuchi,* Materials Science and Engineering, Univ. Of Maryland*; E. Fuller, A. Talin,* Sandia National Laboratories*; M. Jugovac, P. Moras,* Istituto di Struttura della Materia, Consiglio Nazionale delle Ricerche, Italy*; A. Mascaraque,* Dto. Fïsica de Materiales, Univ. Complutense de Madrid, Spain*; E. Garcia Michel,* Dto. Física Materia Condensada, Univ. Autonoma de Madrid, IFIMAC (Condensed Matter Physics Center), Spain

Despite the great interest in LiCoO$_2$ (LCO) and related materials for their applications in batteries, catalysis and resistive memory devices, uncertainties regarding the valence band structure, charge compensation and the nature of the insulator-to-metal transition (IMT) remain controversial [1][2]. In addition, the use of chemical and electrochemical methods on heterogeneous materials, including cathode binders and solid electrolyte interfaces, pushes research further away from a fundamental understanding of the processes involved in ion deintercalation.

We have developed a surface science-based approach to vary the Li content, based on Ne$^+$ sputtering and performed entirely in situ under ultra-high vacuum (UHV) conditions on epitaxial LCO thin films, without interactions between the material and any electrolyte.

This has allowed us to obtain high-resolution angle-resolved photoemission (ARPES) data of the valence band structure in LCO for a wide range of Li molar fractions, directly observing the IMT at x=0.95 and the regions of phase coexistence and phase dominance. X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) were used to characterize the material during Li deintercalation and to investigate the mechanisms of charge compensation in the absence of electrolyte. Li removal is accompanied by the formation of Co^{4+} from the initial Co^{3+} in the LCO structure. Oxygen holes were also observed, related to the hybridization of Co 3d and O 2p orbitals. The valence band was interpreted using reported theoretical calculations [3] and limited previous experimental work [4]. We identify the Co 3d t_{2g} energy levels as those involved in the IMT and locate the valence band maxima (VBM) with a clear 3-fold symmetry and band renormalization, suggesting a Mott character of the transition.

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5:00pm **SS+AS+TF-MoA-11 Nanoscale Hydrogen Detection Using Time-of-Flight Secondary Ion Mass Spectrometry**, *B. Paudel, J. Dhas, M. Choi, Y. Du, **Zihua Zhu**,* Pacific Northwest National Laboratory

Hydrogen in materials attracts tremendous interest as its incorporation leads to significant alterations in structure, composition, and chemistry, which in turn impacts functional properties. Additionally, it has been integral to nuclear fusion reactors and is regarded as the major source of clean energy. However, nanoscale manipulation and characterization of hydrogen in materials are challenging as only a selected few analytical technique can readily detect hydrogen, among which time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a unique and powerful technique due to its excellent detection limit along with decent spatial and depth resolutions. In our lab, ToF-SIMS has been used for hydrogen detection for more than 15 years, and it became more and more important in the last several years. In this presentation, we will discuss, using selected examples, how the detection and quantification of hydrogen in materials by ToF-SIMS has been utilized to reveal the hydrogenation/protonation-induced novel functional states in different classes of materials along with some tricks on sample preparation, optimized experimental conditions to achieve reasonable detection limits of hydrogen, and future prospects. We emphasize the unique capabilities of ToF-SIMS which can potentially unlock new functional states and answer some outstanding scientific questions in materials science.

Biomaterial Interfaces Division
Room B117-119 - Session BI+AS+PS-TuM
Biomolecules and Biophysics at Interfaces

Moderators: Christopher So, Naval Research Laboratory, **Markus Valtiner**, Vienna University of Technology, Austria

8:00am **BI+AS+PS-TuM-1 Probing Protein Structure on Nanoplastic Surface by Sum Frequency Scattering**, ***Akriti Mishra**, T. Weidner,* Aarhus University, Denmark

The safe use of nanoparticle protein conjugates in biomedical applications like disease diagnosis, drug delivery, biosensing, etc. depends on the efficacy and stability of these conjugates in body fluids. To date, several analytical techniques like UV-Vis, dynamic light scattering, Fourier transform infrared spectroscopy, circular dichroism, nuclear magnetic resonance, etc. have been used to study the interaction of proteins on nanoparticle surface. Since most of the techniques can not differentiate between the surface bound and the free proteins in solution, it becomes impossible to gather any information about the interfacial proteins. The confirmation of a protein after adsorption on nanoparticle surface can be drastically different from that in solution, which may hamper or amend the activity and function of proteins. Surface sensitive sum frequency scattering (SFS) stands out best in this case since it selectively probes the vibrational modes of the adsorbed analytes on any interface. Sum frequency generation from flat interfaces has been successfully shown to provide rich information about the structure, order, and composition of molecules at the interface. Recently, our group has shown that SFS can effectively probe the structure and orientation of model peptides at nanoscopic oil particle surfaces.1 We will here discuss how also complex human corona proteins can be probed on particle surfaces. We focus on alpha synuclein (aS) interactions with nanoparticles relevant for medical applications and environmental nanoplastics. aS is a 14 kDa intrinsically disordered protein known to form amyloids called Lewy bodies, which can propagate across the neurons to induce Parkinson's disease (PD). Using SFS we follow how aS binds and folds on polymer nanoparticle surfaces. SFS spectra in the amide I region strongly suggest that aS folds into beta sheet and fibrillated structures at the nanointerfaces This is in contrast with flat surfaces, where monomers and helical folds dominate based on reflection SFG experiments.2 We believe, aS binding to the nanoparticles leads to close packing of aS monomers, which leads to the formation of beta sheet and fibrillar type structures.

Fig 1. Schematic of the SFS experiments to follow the binding of aS to polymer nanoparticles particles and the corresponding SFS spectrum

References:

1.) Thaddeus W. Golbeck, Kris Strunge, Adam S. Chatterly, and Tobias Weidner* J. Phys. Chem. Lett. 2022, 13, 10858-62.

2.) Kris Strunge, Tucker Burgin, Thaddeus W. Golbek, Steven J. Roeters, Jim Pfaendtner and Tobias Weidner* Umbrella-like helical structure of alpha-synuclein at the air-water interface observed with experimental and theoretical sum frequency generation spectroscopy, in preprint.

8:20am **BI+AS+PS-TuM-2 The Structure of Alpha-Synuclein at Lipid Interfaces Determined by Experimental and Theoretical Sum Frequency Generation Spectroscopy**, *K. Strunge, K. Pedersen, T. Golbek, M. Brgenhøj, D. Otzen, B. Schiøtt, **Tobias Weidner**,* Aarhus University, Denmark

The aberrant folding of α-synuclein (αS) into amyloid aggregates is associated with Parkinson's disease. It has been shown that the refolding into oliogomers and harmful fibrils can be catalyzed by lipid-membrane surfaces. Despite the importance of lipid interactions, the 3D-structure of lipid-membrane bound αS, and thereby, the mechanism of the catalysis process, is still not known at the molecular level. Here, we report interface-specific sum-frequency generation (SFG) experiments revealing how monomeric αS binds, folds and orients at anionic lipid membranes. Since SFG is inherently surface specific and unbond proteins are not detected, the experiments can be performed at high αS concentrations, far beyond previous structural studies. To interpret the experimental SFG data and develop a high fidelity structural model of the aS binding motif, we developed an analysis method in which out-of-equilibrium molecular-dynamics (MD) simulations are linked to excitonic amide-I SFG spectra calculations. 10s of thousands of theoretical spectra calculated for frames of extensive MD simulations are evaluated pooled for their experimental fitness to determine the structure of aS binding at low, physiological and pathological aS concentrations. We find that at low and physiological αS concentrations, the protein binds in a flat geometry, while at elevated, pathological concentrations, a transition to an upright αS binding pose occurs. This upright conformation promotes lateral interactions and likely explains how protein concentrations can catalyze the formation of αS amyloids.

8:40am **BI+AS+PS-TuM-3 Lubricant Viscosity Affects the Antifouling Activity of PFPE Based SLIPS Coatings**, ***Onur Özcan**, J. Karthäuser, R. Kopecz, A. Gelhar, A. Rosenhahn,* Ruhr-Universitat Bochum, Germany

Settlement of organisms on submerged surfaces can enhance the spread of life-threatening infections.[1] Therefore it is desired to identify methods for the prevention of biofilm formation. The omniphobic properties of slippery liquid infused porous surfaces (SLIPS) have been shown to provide outstanding protection against biofouling, icing, corrosion and to be repellent against complex liquids like blood.[2] In this study, we examine the fouling behavior of E. coli, P. fluorescence, and B. subtilis on seven different superhydrophobic perfluoropolyether (PFPE) urethane methacrylate-based SLIPS with varying lubricant viscosities. The polymers were fabricated following our previously published grafting-through protocolby which superhydrophobic micro-structured porous PFPE matrices could be obtained by adding cychlohexanol as pore forming agent to the monomer mixture.[3,4] The coatings were incubated in an excess of seven different lubricants of varying viscosities to obtain SLIPS. In dynamic attachment assays we were able to show the antifouling capabilities of these SLIPS with organism reductions of up to 90% compared to the dry, smooth, and hydrophobic butyl methacrylate references. Our results further revealed critical species-specific settlement on the coatings that depended on the viscosity of the incorporated liquid, highlighting the relevance of the choice of the lubricant in the design of low-fouling SLIPS.

[1] M.V. Horton, J. E. Nett, Curr. Clin. Microbiol. Rep. 2020, 7, 51-56. [2] T.-S. Wong, S. H. Kang, S. K. Y. Tang, E. J. Smythe, B. D. Hatton, A. Grinthal, J. Aizenberg, Nature 2011, 477, 443-447. [3] F. Koschitzki, R. Wanka, L. Sobota, J. Koc, H. Gardner, K. Z. Hunsucker, G. W. Swain, A. Rosenhahn, ACS Appl. Mater. Interfaces. 2020, 12, 34148-34160. [4] N. Keller, J. Bruchmann, T. Sollich, C. Richter, R. Thelen, F. Kotz, T. Schwartz, D. Helmer, B. E. Rapp, ACS Appl. Mater. Interfaces, 2019, 11, 4480-4487.

9:00am **BI+AS+PS-TuM-4 Orientation of the Dysferlin C2A Domain is Responsive to the Composition of Lipid Membranes**, *A. Carpenter,* Oregon State University*; S. Roeters, T. Weidner,* Aarhus University, Denmark*; **Joe Baio**,* Oregon State University

Dysferlin is a 230 kD protein that plays a critical function in the active resealing of micron-sized injuries to the muscle sarcolemma by recruiting vesicles to patch the injured site via vesicle fusion. Muscular dystrophy is observed in humans when mutations disrupt this repair process or dysferlin is absent. While lipid binding by dysferlin's C2A domain (dysC2A) is considered fundamental to the membrane resealing process, the molecular mechanism of this interaction is not fully understood. By applying nonlinear surface-specific vibrational spectroscopy, we have successfully demonstrated that dysferlin's N-terminal C2A domain (dysC2A) alters its binding orientation in response to a membrane's lipid composition. These experiments reveal that dysC2A utilizes a generic electrostatic binding interaction to bind to most anionic lipid surfaces, inserting its calcium binding loops into the lipid surface while orienting its β-sheets 30–40° from surface normal. However, at lipid surfaces, where PI(4,5)P2 is present, dysC2A tilts its β-sheets more than 60° from surface normal to expose a polybasic face, while it binds to the PI(4,5)P2 surface. Both lipid binding mechanisms are shown to occur alongside dysC2A-induced lipid clustering. These different binding mechanisms suggest that dysC2A could provide a molecular cue to the larger dysferlin protein as to signal whether it is bound to the sarcolemma or another lipid surface.

9:20am **BI+AS+PS-TuM-5 Probing the Interfacial Action of *Thermomyces Lanuginosus* Lipase at Lipid Surfaces with Vibrational Sum Frequency Spectroscopy – from Monolayers to Emulsions**, ***Khezar Saeed**, K. Strunge, T. Golbek, T. Weidner,* Aarhus University, Denmark

Lipases are a diverse class of biologically important enzymes with a key role in the digestion of dietary fats. The general ability to catalyse triacyl glyceride hydrolysis also enables their application to a wide variety of systems outside of the digestive tract, including transesterification, enantioselective synthesis and as an additive to laundry detergents. Key to their efficacy is the phenomenon of interfacial activation. For lipases this almost universally involves the "opening" of a lid domain upon interaction with a lipid surface, revealing a hydrophobic region containing the active site. The lipase derived from the *Thermomyces lanuginosus* fungus (TLL) is used extensively on an industrial scale as an additive to laundry detergents. As such significant effort has been expended to genetically engineer improvements to the lipase function, with particular attention paid to this lid region. Gaining a deeper understanding of the interfacial activation mechanisms of such lipases could inform the design of improved enzymes in the future.

The inherent surface sensitivity of vibrational sum frequency generation (VSFG) spectroscopy can provide the required molecular level information to further our understanding of the interfacial activation of TLL. VSFG spectroscopy relies on the selection rules associated with frequency mixing of high power visible and infrared laser beams, resulting in a vibrational spectrum of solely the interfacial region. Three key results are presented here:

(i)The TLL-catalysed reaction at the air/triglyceride/water interface can be monitored by reflection VSFG spectroscopy, showing loss of ester carbonyl modes and appearance of carboxylate stretching modes of the fatty acid products.

(ii)Comparison of experimental and predicted VSFG spectra of the amide I band are used to interpret structural changes in the lid domain of TLL upon interaction with a hydrophobic surface.

(iii)Specially formulated emulsions allow further analysis using our new angle-resolved sum frequency scattering spectrometer, showing the first example of reaction dynamics at a particle surface probed by vibrational sum frequency scattering spectroscopy.

This work highlights the utility of VSFG spectroscopy for studying interfacial reactions. Not only does it offer a label-free method of following surface reactions, but it also provides structural and orientational information on interfacial species when combined with appropriate simulations. Furthermore, the results from the sum frequency scattering spectrometer open the door to studying a whole new class of chemical systems at particle surfaces with as yet unseen levels of molecular detail for such systems.

11:00am **BI+AS+PS-TuM-10 An *in Situ* Look at Interfacial Controls on Nucleation, Self-Assembly, and Crystal Growth in Biomolecular and Biomimetic Systems***, **Jim De Yoreo**,* Pacific Northwest National Laboratory **INVITED**

From harvesting solar energy to capturing CO_2 to purifying water, living organisms have solved some of the most vexing challenges now faced by humanity. They have done so by creating a vast library of proteins and other macromolecules that can assemble into complex architectures and direct the mineralization of inorganic components to produce materials characterized by a hierarchy of structure. While the high information content contained within the intricate sequences of the proteins is crucial for accomplishing these tasks, self-assembly and mineralization are nonetheless constrained to proceed according to the physical laws that govern all such processes, even in synthetic systems. An understanding of the mechanisms by which biological systems successfully manipulate those laws to create hierarchical materials would usher in an era of materials design to address our most pressing technological challenges. In this talk, I will present the results of recent research using in situ atomic force microscopy and in situ transmission electron microscopy to directly observe interfacial structure, protein self-assembly, and nanocrystal formation in biomolecular and biomimetic systems, including protein-directed nucleation of calcium carbonate and calcium phosphate and mineral-directed nucleation of two-dimensional protein assemblies. The results elucidate the mechanisms by which the interface between biomolecules and materials directs nucleation, self-assembly and crystal growth, leading to unique materials and morphologies. The results reveal the importance of surface charge, facet-specific binding, solvent organization near interfaces, and, more generally, the balance of protein-substrate-solvent interactions in determining how ordered materials emerge in these systems.

11:40am **BI+AS+PS-TuM-12 the Surface Chemistry of Gecko Toe Pads***, **Mette Heidemann Rasmussen**, K. Holler,* Department of Chemistry, Aarhus University, Denmark*; J. Baio,* School of Chemical, Biological and Environmental Engineering, Oregon State University*; C. Jaye, D. Fischer,* National Institute of Standards and Technology, Gaithersburg*; S. Gorb,* Functional Morphology and Biomechanics, Zoological Institute, Kiel University, Germany*; T. Weidner,* Department of Chemistry, Aarhus University, Denmark

Geckos can climb nearly all surface and are able to cling to walls and ceilings using their toe pads. The gecko adhesion mechanism has been debated over the past years. Current models include van der Walls, hydrophobic and acid-base interactions. Even though the adhesion mechanism of the spatulas has been studied in detail, the surface chemistry involved in the gecko adhesion mechanism is unclear. What is the structure of the supporting proteins within the spatula at the very tips of the setae within the gecko toe pad? What is the role of lipids in the adhesion process? Understanding the surface chemistry of the adhesion of the gecko toe pads gives insight into this highly specialized biological interface, and give clues for materials scientists aiming at mimicking the gecko adhesion mechanisms. Using near edge X-ray absorption fine structure (NEXAFS) imaging and spectroscopy we have studied the structure and order of the molecules at the outermost surface layer of gecko toe pads. We show that the keratin molecules within the spatulas are highly organized and adopt a flat, strand-like geometry, which may support the stability and adaptability of gecko setae (1). We will also discuss evidence showing that a nanometer-thin ordered lipid layer is covering the beta proteins (2).

1. Structure of Keratins in Adhesive Gecko Setae Determined by Near-Edge X-ray Absorption Fine Structure Spectromicroscopy. J Phys Chem Lett. 2022 Mar 10;13(9):2193–6.

1. Evidence that gecko setae are coated with an ordered nanometre-thin lipid film. Biology Letters. 18(7):20220093.

12:00pm **BI+AS+PS-TuM-13 All-Atom Simulations of Peptide Aggregation: Understanding and Predicting Biopolymeric Morphologies***, A. Kwansa, A. Cannon,* North Carolina State University*; **Yaroslava Yingling**,* 911 Partners Way, Engineering Building I, Campus Box 7907

The self-assembly and aggregation of partly or completely disordered peptides have emerged as crucial areas of research with broad implications in therapeutics, supramolecular assembly, and functional biomaterials. Understanding the intricate processes underlying the self-assembly and aggregation of these proteins is essential for harnessing their functional properties and expanding their applications. Simulations can be used to isolate the importance of the interplay between aggregate morphology and secondary structure formation. However, most of the simulation's studies investigate either single peptide in solution or several short peptide analogues. We used large-scale all-atom MD simulations to investigate the structure of hydrated peptide aggregates in detail. Two example systems were investigated, reflectin and elastin-like peptides (ELP). Reflectin proteins, found in cephalopods, play a pivotal role in dynamic coloration for camouflage and communication. On the other hand, ELP proteins possess unique thermoresponsive properties, making them attractive for drug delivery systems, tissue engineering, and biomaterial design. We found significant differences between the structure of a single polypeptide in water and the structure of peptide within the aggregate. Overall, the aggregation process is driven by the formation of peptide–peptide interactions whereas the average hydration of peptides remains almost the same between dissolved and aggregated states. Even though the aggregation is driven by hydrophobic interactions, aggregate has no hydrophobic core and contains many water molecules. Overall, our findings provide an insight into the sequence-dependent structure of aggregates and molecular behavior of individual peptides during aggregation.

Chemical Analysis and Imaging of Interfaces Focus Topic
Room A105 - Session CA+AS+LS+LX+MN+SE+SS-TuM

Novel Developments and Applications of Interfacial Analysis

Moderators: Andrei Kolmakov, National Institute of Standards and Technology (NIST), **Slavomir Nemsak**, Advanced Light Source, Lawrence Berkeley National Laboratory

8:00am **CA+AS+LS+LX+MN+SE+SS-TuM-1 Hypervelocity Nanoprojectile Impacts on Graphene, Graphene-Solid/Liquid Interphases: From Mechanisms of Interaction/Ejection to Practical Applications***, **Dmitriy Verkhoturov**,* Texas A&M University*; S. Lee,* Mayo Clinic*; M. Eller,* California State University Northridge*; M. Gołuński, S. Hrabar,* Jagiellonian University, Poland*; S. Verkhoturov,* Texas A&M University*; Z. Postawa,* Jagiellonian University, Poland*; A. Kolmakov,* National Institute for Science and Technology (NIST)*; A. Revzin,* Mayo Clinic*; E. Schweikert,* Texas A&M University **INVITED**

Presented here are the experiment and theory on processes accompanying the impacts of C_{60} and Au_{400} projectiles (~1 keV/atom) on graphene/matter interphases. A variety of targets were used: a) free standing graphene, b) molecules and extracellular vesicles (EVs) deposited on free standing graphene, c) interphases graphene-solids/liquids, d) EVs deposited on functionalized monocrystals.

Two custom-built Cluster ToF secondary ion mass spectrometry (SIMS) devices with similar parameters were used. The experiments were run in the event-by-event bombardment/detection mode where the regime of bombardment is super-static[1]. The analyzed surfaces were bombarded at the rate of ~1000 impacts/sec with 1-6×10^6 impacts collected on a surface area of 50-500 µm in diameter. This regime allows acquisition of individual mass spectra for each impact, thus allowing the comparison of experimental data with MD simulations at the level of single projectile impacts. The method allows detection of ejecta in reflection (3D case) and transmission (2D case) directions.

The mechanisms of ejection from 2D and 3D materials (including graphene-solid/liquid interphase) are different. For example, in the case of C_{60} impacts on a molecular layer deposited on graphene (2D case) the mechanism of ejection is described with the “trampoline” model[2]. For the 3D case of graphene-solid/liquid interphase, graphene suppresses the ejection of molecules. The compression of matter in the excitation volume around the impact is not sufficient to destroy the graphene[3].

Our method allows to test individual nano-objects. A biological example is EVs. There were anchored on functionalized Si and graphene substrates, with the EVs labeled with antibodies carrying lanthanide tags (Ab@Ln) for normal hepatic and liver cancer markers. Up to four Ab@Ln tags could be detected simultaneously, enabling analysis of population heterogeneity with single EV resolution and to distinguish between normal and cancer EVs based on surface marker expression. Using co-localization of cancer biomarkers, it is possible to find small subpopulation of EVs originating from cancerous cells potentially allowing for early cancer detection. The sensitivity of the method can be increased several folds via transmission configuration where ejecta are emitted and detected in the forward direction. In this case nano-objects, such as EVs, are anchored on graphene oxide, a 2D material.

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Acknowledgements: NSF Grant CHE-1308312, NIH Grant R01 GM123757-01,

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8:40am **CA+AS+LS+LX+MN+SE+SS-TuM-3 Applying *in Situ* Bias During TOF-SIMS Analysis to Investigate Ion Migration in Perovskite Devices*, Steven Harvey,*** National Renewable Energy Laboratory*; I. Gould,* University of Colorado, Boulder*; D. Morales, M. McGehee,* University of Colorado Boulder*; A. Palmstrom,* National Renewable Energy Laboratory

Metal Halide Perovskite Photovoltaics have the potential to be a game-changing technology in photovoltaics, with low cost solution processing inherent to the technology and a rapid progress in device efficiency and stability. Understanding ion migration in these materials has lead to improvements in both efficiency and reliability, and further understanding of these phenomena is of great importance.

Time of flight secondary ion mass spectrometry is well suited to provide unique insight for this class of materials, as it can reveal the distribution of both the organic and inorganic components of a device stack (both through the depth as well as laterally with 2-D and 3-D imaging). We will briefly cover our past work on technique development for this class of materials, before presenting new work where an *in situ* electrical bias was placed on a perovskite device while under investigation with TOF-SIMS. This was completed with simple commercial off the shelf components in an ION-TOF TOF-SIMS V instrument and could be easily implemented on other instruments. A device stack of glass / ITO / Me-4PACz / DMA0.1FA0.6Cs0.3Pb(I0.8Br0.2)3 / LiF (1 nm) / C60 (30 nm) / SnOx (15 nm)/Au (20 nm) was used for this study. An electrical bias was applied between the top gold contact and the bottom ITO contact during TOF-SIMS measurements. By applying a +0.75V and -0.75V forward and reverse bias to the device, a driving force for negatively charged halide ions is created to migrate towards the back or front of the device, respectively. The *in-situ* data shows the halide ion migration towards the back ITO contact after the forward bias is applied. The negative bias was then applied and the halide ions migrate back towards the front of the device and return to the original unbiased state. In both cases the formamidinium and lead traces do not show similar migration, showing only the charged species in the device are affected by the bias. The results show a framework that can be used for further study. Potential complications with the analysis of this type of data will be discussed.

9:00am **CA+AS+LS+LX+MN+SE+SS-TuM-4 Oxidation of a Single Fe Nanoparticle at the Nanoscale and Real-Time by Operando Atom Probe*, Sten V. Lambeets,*** Pacific Northwest National Laboratory*; N. Cardwell, I. Onyango,* Washington State University*; T. Visart de Bocarmé,* Université libre de Bruxelles, Belgium*; J. McEwen,* Washington State University*; D. Perea,* Pacific Northwest National Laboratory

Physics governing surface chemical reactions and interfaces involved in heterogeneous catalysts fundamentally depends on the synergistic interactions between reactive gases and specific surface structures. Surface science techniques are continuously evolving to help bridge knowledge gaps between fundamental research and real-world applications. In the past decade, an increasing number of analytical techniques successfully achieved their evolution towards an in situ and operando version of themselves, and recently such approaches are being developed for atom probe microscopy (APM) techniques. In this work, we will present the recent advances in the conversion of Atom Probe Tomography (APT) to study surface dynamics of O_2/Fe using two different APM techniques and modifications: Field Ion Microscopy (FIM), and Operando Atom Probe (OAP).

APM techniques are capable of imaging the apex of sharp needles with nanometric lateral resolution, which can be seen as model nanoparticles. FIM is used to image such needles with atomic resolution and to identify the crystal orientation along with the local surface reaction dynamics during oxygen interaction with Fe. The resulting FIM image corresponds to a stereographical projection of the apex and allows the identification of the crystal orientations with atomic resolution. Regular APT, from which the OAP derives, relies on the thermally assisted field evaporation of positively charged ions from a needle shaped specimen. In regular use, the APT is performed in an Ultra High Vacuum (<10^{-11} mbar) while the sample is cooled at 50K. The OAP modification consists of performing the atom probe analysis in the presence of reactive gas at 300 K.

Once the FIM characterization is complete the sample is maintained at 300K before starting APT analysis and introducing 1.1×10^{-7}mbar of pure O_2. As soon as the O_2 is introduced, we can measure the surface formation of Fe oxides by monitoring the local concentration of Fe_2O^{n+} ion species extracted from the surface over time. We can track the local concentration over the different surface regions in real time. We observe the progressive surface oxidation starting from open facets structures, such as Fe{222} and Fe{112}, towards the central Fe(011) and the Fe{024} which show significantly higher resistance toward oxidation. The combination of the different concentrations allows us to reconstruct the full movie of the surface oxidation in real-time. However, since the measurements are performed in the presence of very strong electric fields (>10 V/nm), it is necessary to discuss the potential influences of it on the system as well.

9:20am **CA+AS+LS+LX+MN+SE+SS-TuM-5 Reporting Interfaces: Unconventional Excitation of Interfaces Enables Exquisite Gas Sensing Toward Our Sustainable Future*, Radislav Potyrailo,*** GE Research **INVITED**

As our society is developing solutions for more sustainable types of energy, the need for reliable, yet affordable tools for monitoring of emissions of greenhouse and other gases in urban and industrial environments is a substantial undertaking for two main reasons. First, to achieve a desired accuracy, existing gas monitoring solutions in complex backgrounds utilize traditional analytical instruments. While their mathematical design principles provide needed independent response outputs, their hardware design principles do not allow cost-effective ubiquitous implementations. Second, all gas sensors based on interface-driven interactions between gases of interest and sensing materials are single-output devices. By their original design principles from early last century, these sensors operate well only when levels of interfering gases are low. Once levels of interfering gases increase, existing sensors lose their accuracy because of competing interactions between the sensor interface and numerous interfering gases versus a gas of interest.

In this talk, we will present gas sensors that we built following mathematics of traditional analytical instruments but with our own different types of independent variables for detection of multiple gases with enhanced accuracy and stability. These sensors are multivariable gas sensors where independent response outputs are provided by our unconventional methodologies of excitation of interfaces between a sensing material and different ambient gases. We will show that our approach results in a reliable differentiation of one or more analyte gases in complex backgrounds of interfering gases with an individual multivariable gas sensor. This exquisite (i.e., accurate and reliable) gas sensing provides an affordable technical solution for monitoring of emissions of greenhouse and other gases in urban and industrial environments. Such technical solution is mathematically not feasible using conventional single-output sensor designs. We will also show that such multivariable gas sensors have the ability for self-correction for sensor drift. Our approach for the multi-gas detection and drift self-correction should allow implementations of gas sensors in diverse applications that cannot afford weekly, monthly, or quarterly periodic maintenance, typical of traditional analytical instruments.

11:00am **CA+AS+LS+LX+MN+SE+SS-TuM-10 A "Simple" Approach to Combine Electrochemistry and Operando Near Ambient Pressure XPS Studies***, F. Mirabella, **Paul Dietrich**, A. Thissen,* SPECS Surface Nano Analysis GmbH, Germany **INVITED**

Electrochemical water splitting is an environmentally friendly technology to store renewable energy in the form of chemical fuels. Among the Earth-abundant, first-row transition metal-based catalysts, Ni and Fe oxides have shown promising performances as effective and low-cost catalysts of the oxygen evolution reaction (OER) in alkaline media. Notably, their structure evolves under oxygen evolution operating conditions with respect to the as-prepared catalysts but these changes and consequently the active sites have not been identified yet due to the difficulties associated with surface analysis measurement under working conditions (*operando*).

In this presentation, we will demonstrate the enormous potential of laboratory NAP-XPS for investigations of solid-liquid interfaces in electrochemical systems at elevated pressures (≤ 25 mbar), also illustrating the ease of use of this specific setup. We will show a versatile three-electrodes electrochemical setup that allows for operando studies of solid-electrolyte interfaces, i.e., of nickel oxide foils as cathode for OER in alkaline environment as a simple laboratory NAP XPS experiment.

11:40am **CA+AS+LS+LX+MN+SE+SS-TuM-12 Recent Developments in Probing Buried Interfaces Using Standing-Wave Photoelectron Spectroscopy***, **Slavomir Nemsak**,* Lawrence Berkeley Lab

Standing-wave photoelectron spectroscopy of multi-layer structures proved to be a very powerful technique for probing solid/solid, but also solid/liquid and solid/gas interfaces. Its superior depth selectivity and non-destructive nature were crucial to answer key questions in problems spread over several scientific fields, such as emergent phenomena at complex oxide interfaces [1], artificial multiferroics [2], adsorption mechanisms in liquids [3], corrosion [4], and electrocatalysis [5].These achievements were only possible thanks to innovative approaches both in experiments and analyses, including development of X-ray optical simulations package [6] and its coupling with the black-box optimizer [7]. In this talk I will introduce novel tools and approaches for standing-wave experiments and I will highlight some of the recent applications [8,9,10].

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[9] G. Conti et al., *Journal of Micro/Nanopatterning, Materials, and Metrology* **20**, 034603 (2021).

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12:00pm **CA+AS+LS+LX+MN+SE+SS-TuM-13 The Influence of Surface Structure and Electrostatics on Measuring Unoccupied Electronic States via Low Energy Inverse Photoemission Spectroscopy (LEIPS)***, **James Johns**,* Physical Electronics USA

A material's energetic distribution of electronic states near the fermi level is a key physical property for determining how it behaves in electronic, chemical, and optical applications.Photoemission has long been the gold standard for measuring the occupied electronic states below the Fermi level and is one of the most common surface science techniques worldwide.Inverse photoemission (IPES), the related process whereby an electron is absorbed at the surface and a photon is emitted, is similarly a very powerful tool for measuring the unoccupied electronic states. Unfortunately, the intrinsically lower rate for IPES and technical hurdles related to relevant photodetectors has historically necessitated the use of electron sources with sufficient energy to damage all but the most chemically robust surfaces.

The availability of narrow bandpass optical filters at UV photon energies between 3.5 and 6 eV over the past decade have enabled the development and commercialization of Low Energy Inverse Photoemission Spectroscopy (LEIPS)[1,2].Efficient detection of low energy UV photons (lower than traditional IPES at 9-10 eV) enables the use of low energy electrons (below 5 eV) which avoid damaging sensitive materials including organics.This key innovation has revitalized interest in IPES because the technique can now be applied to molecular materials and interfaces relevant to wide range of applications *e.g.* batteries, photovoltaics, organic semiconductors and OLEDs, chemical sensors.Furthermore, optical UV filters also improve the energy resolution, further enhancing the appeal of LEIPS over traditional IPES.

Like any surface science technique, the quality of LEIPS data depends on both the instrumentation and sample preparation. Here, I will discuss the material requirements and limitations for successful LEIPS measurements, several of which differ from more common techniques such as XPS, SPM, or electron microscopy.I will also present LEIPS data from taken at the interface between two metals and explain those results using calculated trajectories of the electron beam.Finally, I will illustrate a key difference between LEIPS, which probes the true unoccupied electronic density of states, and optical methods, such as optical spectroscopy or EELS which measure the joint density of states, by presenting LEIPS spectra of an excitonic 2D material.

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[2]Lida, S.; Terashima, M; Mamiya, K; Chang, H. Y.; Sasaki, S; Ono, A; Kimoto, T; Miyayama, T; "Characterization of cathode-electrolyte interface in all-solid-state batteries using TOF-SIMS, XPS, and UPS/LEIPS" *J. Vac. Sci. & Tech. B*, **39**, 044001, (2021)

Surface Science Division
Room D136 - Session SS+2D+AS+HC-TuM
Oxide and Chalcogenide Surfaces and Interfaces

Moderators: Rachael Farber, University of Kansas, **Gareth Parkinson**, TU Wien

8:00am **SS+2D+AS+HC-TuM-1 ViPErLEED: LEED-*I*(*V*) Made Easy***, **Alexander Michael Imre**[1],* TU Wien, Austria*; F. Kraushofer,* TU Munich, Germany*; T. Kißlinger, L. Hammer,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; M. Schmid, U. Diebold, M. Riva,* TU Wien, Austria

Most surface science laboratories are equipped with a low-energy electron diffraction (LEED) setup. LEED patterns provide quick, qualitative insight into surface structure and ordering. However, the diffracted electron beams contain a large amount of additional structural information which is often ignored. By studying the diffraction intensities as a function of incident electron energy [LEED-*I*(*V*)], it is possible to quantitatively compare experimentally observed surfaces with structural models.

Despite the clear need for such a direct experiment-to-theory comparison, LEED-*I*(*V*) is only routinely used by few specialized groups. A main obstacle for widespread adoption is that existing solutions for LEED-*I*(*V*) analysis and simulation are time-consuming and hard to use for scientists who are not already experts in the field.

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

To resolve this issue, we have developed the Vienna Package for Erlangen LEED (ViPErLEED) – a package of three independent but complementary tools for easy LEED-*I*(*V*) acquisition and analysis. All parts of ViPErLEED will be released as open source at the time of publishing:

1. **Electronics:** We provide schematics and control software for electronics, which allows users to easily and cheaply upgrade most existing LEED setups for acquiring high-quality LEED-*I*(*V*) data. These ViPErLEED electronics are based on an Arduino microcontroller and can be home-built from off-the-shelf components. The associated control software synchronizes with the camera and automates the experiment.
2. **Spot-tracker:** ViPErLEED provides a plugin for the public-domain image processing program ImageJ, for spot tracking and extraction of LEED-I(V) spectra from series of raw diffraction images. The automatically extracted I(V) curves can be used for further analysis or as a fingerprint of the surface surface. The plugin package also provides user-friendly options for examination, selection and smoothing of the *I*(*V*) data.
3. **Simulation software:** For structure analysis, we introduce a Python package for calculation of LEED-*I*(*V*) spectra and structure optimization. This software is based on the established TensErLEED package and extends its functionality while still making it easy for new users to get started with the technique. It uses standard file formats for the surface structure, provides automated symmetry detection, and requires just a handful of parameters for running a structure determination.

8:20am **SS+2D+AS+HC-TuM-2 Quasicrystal-like Ordering of the $La_{0.8}Sr_{0.2}MnO_3$(001) Surface***, **Erik Rheinfrank**, G. Franceschi, L. Lezuo, M. Schmid, U. Diebold, M. Riva,* TU Wien, Austria

Lanthanum-strontium manganite ($La_{0.8}Sr_{0.2}MnO_3$, LSMO) is a perovskite oxide used as a cathode material in solid oxide fuel cells, which convert chemical energy to electrical energy. To gain deeper insights into the reaction mechanisms, it is important to understand the structure of the surface at the atomic scale. To this end, we grow atomically flat single-crystalline LSMO thin films on Nb-doped $SrTiO_3$ (STO) substrates via pulsed laser deposition (PLD). Previously, this has been achieved for the (110) orientation.[1,2. Here, we use a similar approach on the (001) surface that is commonly used for oxide-based electronics and spintronics. The as-grown films have a MnO_x terminated surface that shows a 4-fold symmetric structure in low-energy electron diffraction (LEED), best explained by a set of four basis vectors reminiscent of quasicrystals. Scanning tunnelling microscopy (STM) and Q+ non-contact atomic force microscopy (nc-AFM) reveal an aperiodic arrangement of tiles with rotation angles of ±26.6° and 90±26.6°, and a Fourier transform consistent with the LEED pattern. As for quasicrystals, the surface has a sharp diffraction pattern despite the lack of translational symmetry.

[1] Franceschi *et al.*, J. Mater. Chem. A, 2020, **8**, 22947-22961

[2] Franceschi *et al.*, Phys. Rev. Materials, 2021, **5**, L092401

8:40am **SS+2D+AS+HC-TuM-3 AVS Graduate Research Awardee Talk: The Selective Blocking of Potentially Catalytically-Active Sites on Surface-Supported Iron Oxide Catalysts***, **Dairong Liu**[1][2], N. Jiang,* University of Illinois - Chicago

The extensive research on ultrathin ferrous oxide (FeO) islands and films over the last few decades has significantly contributed to the understanding of their structural and catalytic properties.One important aspect that has been investigated is the surface properties of ultrathin FeO islands, particularly the role played by the edges of these islands in catalytic reactions, such as CO oxidation. So far, two different types of edge, Fe-terminated edge and O-terminated edge, have been identified in the well-growth FeO island. However, despite this significant progress, the local chemical properties of these two types of edges, including their metal affinity, have remained largely unexplored. Here, we used scanning tunneling microscopy (STM) to study the interaction of Pd and Pt with FeO grown on Au(111). Different Fe affinities for Pd and Pt are demonstrated by the preferential growth of Pd on the Fe-terminated edge and Pt on the O-terminated edge of FeO nanoislands, resulting in selectively blocked FeO edges. In addition to revealing the different metal affinities of FeO edges, our results provide new insights into the edge reactivity of FeO/Au(111) and suggest an approach for controlling the selectivity of FeO catalysts. By comparing the behavior of different edges in the catalysis reaction, the catalytic activity of these edges can be studied solely, thereby sheds light into the future modification of ferrous-based catalysts.

9:00am **SS+2D+AS+HC-TuM-4 Unraveling Surface Structures of Ga-Promoted Transition Metal Catalysts in CO_2 Hydrogenation***, **Si Woo Lee**, S. Shaikhutdinov, B. Roldan Cuenya,* Fritz Haber Institute of the Max Planck Society, Germany

Gallium-containing alloys with transition metals (TM) have recently been reported to be reactive in the selective hydrogenation of CO_2 for methanol synthesis. However, a full understanding of the Ga-promoted catalysts is still missing due to the lack of information about the *surface* structures formed under reaction conditions. In this respect, studies using surface-sensitive techniques applied to well-defined model systems can provide key information to elucidate the reaction mechanism and provide the basis for the rational design of Ga-promoted catalysts.

In this work, we employed *in-situ* Near Ambient Pressure Scanning Tunneling Microscopy (NAP-STM) and X-ray Photoelectron Spectroscopy (NAP-XPS), which make it possible to study surfaces in the reaction conditions, for monitoring the structural and chemical evolution of the Ga-covered Cu surfaces in the CO_2 hydrogenation reaction. NAP-STM images recorded in the reaction mixture revealed temperature- and pressure-dependent de-alloying of the initially formed, well-ordered $(\sqrt{3}\times\sqrt{3})R30°$-Cu(111) surface alloy and the formation of Ga-oxide islands embedded into the Cu(111) surface, exposing GaO_x/Cu(111) interfacial sites. Notably, in our atomically-resolved STM image of Ga-oxide/Cu(111), it is clearly observed that Ga-oxide grows into an ultrathin oxide layer form with $(4\sqrt{3}\times4\sqrt{3})R30°$ superstructure. From NAP-XPS studies on Ga/Cu(111) in the presence of CO_2 and H_2, the formation of formate was observed, and this reaction intermediate was eventually transformed into methoxy at elevated temperatures, representing the final surface-bound intermediate for methanol synthesis. In contrast to Ga-containing Cu catalyst, on the other hand, there was no reaction intermediate at high temperature on the Ga-free Cu(111) surface, demonstrating that further reactions do not occur anymore from chemisorbed $CO_2^{\delta-}$ on Cu surface alone. Therefore, the GaO_x/Cu interface formed under reaction conditions may expose catalytically active sites never considered for this reaction before. We believe that our experimental results shed light on the complex surface structure of Ga-containing catalytic systems, which is only possible to obtain using state-of-the-art experimental techniques under reaction conditions. Only by establishing the atomic structure of the Ga-oxide layer(s) and its interface to the transition metal under working conditions can one bring insight into the reaction mechanism of this methanol synthesis catalyst.

9:20am **SS+2D+AS+HC-TuM-5 Ultrathin Metal Oxide, Nitride and Sulfide Films: Bringing the Well-Known Compounds to a Unit-Cell Thickness***, **Mikołaj Lewandowski**,* NanoBioMedical Centre, Adam Mickiewicz University in Poznań, Poland **INVITED**

Bringing the well-known materials from bulk size to a unit-cell thickness may significantly influence their structure and physicochemical properties. As an example, ultrathin (< 1-nanometer-thick) films of metal/non-metal compounds, such as metal oxides, nitrides or sulfides epitaxially grown on single-crystal supports, are characterized by unique electronic, catalytic and magnetic properties not observed for their bulk counterparts. Such films also exhibit superior structural flexibility, undergoing phase transitions upon exposure to external factors (such as reactive gases or high temperatures) [1,2]. All this makes them promising candidates for applications in various technological fields, including nanoelectronics, spintronics and heterogeneous catalysis.

Within the lecture, I will address the growth, structure and properties of ultrathin metal oxide, nitride and sulfide films, with compounds of iron as exemplary cases. The scanning tunneling microscopy and spectroscopy (STM/STS), low energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), low energy electron microscopy (LEEM) and density functional theory (DFT) results – obtained by my group and our collaborators – provide universal guidelines for designing ultrathin films with desired structure and properties [1–3].

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[1] **AVS Graduate Research Awardee**

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

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11:00am **SS+2D+AS+HC-TuM-10 Optimized Infrared Reflection Absorption Spectroscopy for Metal Oxides: Overcoming Challenges of Low Reflectivity and Sub-Monolayer Coverage***, **Jiri Pavelec**, D. Rath, M. Schmid, U. Diebold, G. Parkinson,* Vienna University of Technology, Austria

Infrared reflection absorption spectroscopy (IRAS) is a wide-spread technique in heterogenous catalysis, and it is an ideal tool for the comparison of real and model catalysts [1]. Most surface science groups perform IRAS studies either directly on metal single crystals, or on (ultra-)thin metal oxide films grown on such samples [2]. Achieving high-quality data from metal-oxide single crystal surfaces is difficult because their low reflectivity necessitates averaging many individual measurements with long acquisition times [3]. The goal of this work was to develop an IRAS setup for studying the adsorption of molecules on model "single-atom" catalysts. Here, the low reflectivity of oxide support is exacerbated by the sub-monolayer coverage of adsorbates on single adatoms. In the contribution, I will present the novel IRAS system we have developed to overcome these two challenges.

The main improvements over commonly-used setups are a high numerical aperture, an optimized optical path, control of the incidence angle range, and high mechanical stability. The high numerical aperture of the optical system leads to an increase in the amount of light reflected from a small single crystal sample. This is achieved by placing both the illumination and collector mirrors inside the UHV chamber close to the sample. To minimize the loss of signal, optimization of the optical path was performed using a ray tracing program. The other limit is the small area on the sample that is covered with adsorbates: in our setup, a molecular beam delivers adsorbates with a spot diameter of 3.5 mm [4]. Infrared light is reflected only from this area.

The reflectivity and absorbance of non-metallic samples varies strongly with incidence angle, and can even change a sign, leading to cancellation. The optimum angle ranges are different for every material. As our setup has a large range of incident angles, we can use this to our advantage: Using two adjustable aperture plates, we can vary the minimum and maximum incidence angle from 49° to 85° to maximize the signal for each single crystal sample. Angle control also allows us to optimize the signal for both p-polarized and s-polarized light independently.

We successfully executed and compared D_2O and CO absorbance measurements on a rutile $TiO_2(110)$ surface, and our results agree with the established literature [3]. By properly selecting the incidence angle range, we achieved a signal-to-noise ratio of ~16 for 1 ML CO adsorbed on TiO_2 with only 150 seconds of measurement time.

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[2] J. Libuda et al., J. Chem. Phys., 114, 10, 2001
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11:20am **SS+2D+AS+HC-TuM-11 VO Cluster-Stabilized H_2O Adsorption on a TiO_2 (110) Surface at Room Temperature***, **Xiao Tong**,* Brookhaven National Laboratory

We probe the adsorption of molecular H_2O on a TiO_2 (110)-(1 × 1) surface decorated with isolated VO clusters using ultrahigh-vacuum scanning tunneling microscopy (UHV-STM) and temperature-programmed desorption (TPD). Our STM images show that preadsorbed VO clusters on the TiO_2 (110)-(1 × 1) surface induce the adsorption of H_2O molecules at room temperature (RT). The adsorbed H_2O molecules form strings of beads of H_2O dimers bound to the 5-fold coordinated Ti atom (5c-Ti) rows and are anchored by VO. This RT adsorption is completely reversible and is unique to the VO-decorated TiO_2 surface. TPD spectra reveal two new desorption states for VO stabilized H_2O at 395 and 445 K, which is in sharp contrast to the desorption of water due to recombination of hydroxyl groups at 490 K from clean $TiO_2(110)$-(1 × 1) surfaces. Density functional theory (DFT) calculations show that the binding energy of molecular H_2O to the VO clusters on the TiO_2 (110)-(1 × 1) surface is higher than binding to the bare surface by 0.42 eV, and the resulting H_2O-VO-TiO_2 (110) complex provides the anchor point for adsorption of the string of beads of H_2O dimers.

11:40am **SS+2D+AS+HC-TuM-12 Synthesis and Multimodal Characterization of Thin-Film Oxides***, **Dario Stacchiola**,* Brookhaven National Laboratory

Thin films of metal oxides exhibit a variety of unique physical and chemical properties leading to broad applications in optics, microelectronics, optoelectronics, superconducting circuits, gas sensors, thermal catalysis, electrocatalysis, and solar energy harvesting. Many metal oxides can form stoichiometric and non-stoichiometric alloys and compounds with each other, commonly known as complex metal oxides. Alloy and compound formation, including growth and process conditions, offer great flexibility for manipulating the lattice, atomic scale structure motifs, and electronic structure to realize desired properties. In order to exploit this potential, knowledge about fundamental processes and atomic level structural information is required. We present here the synthesis and multimodal characterization of mixed-oxide films based on silica and titania, from single layers to complex metal oxides.

1. "Deciphering phase evolution in complex metal oxide thin films via high-throughput materials synthesis and characterization", Nanotechnology 34, 125701 (2023)

2. "Resolving the evolution of atomic layer deposited thin film growth by continuous in situ X-ray absorption spectroscopy", Chem. Mat. 33, 1740-1751 (2021)

3. "First-Principles Study of Interface Structures and Charge Rearrangement at the Aluminosilicate / Ru(0001) Heterojunction" J. Phys. Chem. C 123, 7731–7739 (2019)

12:00pm **SS+2D+AS+HC-TuM-13 Atomic Structure of Reconstructed Al_2O_3(0001) Surface***, J. Hütner, A. Conti,* TU Wien, Austria*; D. Kugler,* CEITEC, Czechia*; F. Mittendorfer, U. Diebold, M. Schmid, **Jan Balajka**,* TU Wien, Austria

Corundum α-Al_2O_3 is an important ceramic widely used in electronics, optical applications, or as catalyst support. Despite its importance, the atomic structure of the most stable (0001) termination has not been conclusively determined. Detailed studies of Al_2O_3 surfaces have been stymied by its insulating nature, preventing the use of many surface science methods.

Structural models based on surface X-ray diffraction (SXRD) [1], and atomic force microscopy (AFM) [2], concluded the $(\sqrt{31} \times \sqrt{31})R\pm9°$-reconstructed Al_2O_3(0001) surface formed upon high-temperature annealing is terminated by one or two layers of metallic Al strained to lattice-match the oxide substrate.

We imaged the reconstructed Al_2O_3(0001) surface with noncontact AFM (nc-AFM) using specifically functionalized tips for chemically-sensitive contrast. In particular, CuO_x terminated tips [3], enabled us to directly identify oxygen and aluminum atoms in the topmost layer.

With the aid of *ab-initio* calculations, we propose a structural model of the $(\sqrt{31} \times \sqrt{31})R\pm9°$-reconstructed Al_2O_3(0001) surface consistent with atomically resolved nc-AFM images and area-averaging spectroscopic data. Unlike prior models, the surface does not contain a metallic Al layer but consists of oxygen and aluminum atoms arranged in similar structural units as reported in thin AlO_x films [4,5].

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Theory for Surface Processes and Spectroscopies Focus Topic
Room B116 - Session TH1+AS+SS-TuM

Introduction and Core-Level Spectroscopies I

Moderators: Gianfranco Pacchioni, Universita' degli Studi di Milano-Bicocca, **John Rehr**, University of Washington

8:00am **TH1+AS+SS-TuM-1 X-Ray Photoelectron Spectroscopy as a Useful Tool to Study Surfaces and Model Systems for Heterogeneous Catalysts*, Hans-Joachim Freund*,** Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany **INVITED**

After a brief introduction into the concepts of photoemission, including multielectron excitations, and a discussion of ways how to extract information on the chemical state of atoms in the non-ionized ground state from the chemical shift in XPS spectra, as well as from the evaluation of the so-called Auger parameter, we present several examples on how appropriate theoretical calculations may be crucial to properly interpret the spectra in terms of initial and final state effects. Four studies on systems representing model systems for heterogeneous catalysts are discussed. The first two refer to simple thin film oxide systems of MgO(100)/Ag(100) supported on metal single crystals.We interpret line widths in terms of vibrational excitations, depending on the thickness of the oxide film, and compare surface core level chemical shifts with those in the bulk, and discus the differences on the basis of ab-initio cluster calculations. The third example refers to chemical shifts of metal/(Pd) atoms adsorbed on bilayer silica films on Ru(0001), and illustrates the use of the Auger parameter to extract initial state chemical shifts. The last example deals with $CeO_2(111)$ surfaces and exemplifies the influence of open shell on the complexity of core level spectra.

8:40am **TH1+AS+SS-TuM-3 X-Ray Absorption and Emission Spectroscopy of Actinide Materials: Electronic Structure Questions from the Experimental Viewpoint*, Bianca Schacherl,*** Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE), Germany **INVITED**

Understanding the electronic structure of one of the most complex element groups in the periodic table, the actinides, has been topic of extensive research in the last decades.

Spectroscopic tools for these investigations are provided by X-ray absorption spectra. Especially the An $M_{4,5}$-edge high-resolution X-ray absorption and emission spectroscopy has proven to be a powerful tool for electronic structure investigations.[1,2]

In this talk it will be demonstrated how newly revealed spectral features can be used for in-depth analyses of the actinide-ligand chemical bond. For model systems, one focus will lie on how the spectra change upon changes in the electronic structure of the actinide compound. It will be highlighted how several theoretical methods can give a valuable input to understand the orgin of the spectral features.[3–7]

This work is supported by the ERC Consolidator Grant "The Actinide Bond" (N°101003292) under the European Union's Horizon 2020 research and innovation program. The Institute for Beam Physics and Technology (IBPT), KIT is acknowledged for the operation of the storage ring, the Karlsruhe Research Accelerator (KARA).

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9:20am **TH1+AS+SS-TuM-5 Towards New Spectroscopic Tools for Detection of Bonding Properties in Radiopharmaceuticals: Application on La Used as a Homolog of Ac*, Tonya Vitova,*** Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal, Germany*; B. Schacherl, H. Ramanantoanina,* Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE), Germany*; M. Benesova,* German Cancer Research Center, Im Neuenheimer Feld 280, 69120 Heidelberg, Germany*; J. Göttlicher,* Karlsruhe Institute of Technology, Institute for Photon Science and Synchrotron Radiation (IPS), P.O. Box 3640, D-76021 Karlsruhe, Germany*; R. Steininger,* Karlsruhe Institute of Technology, Institute for Photon Science and Synchrotron Radiation (IPS), Germany*; M. Haverkort,* Heidelberg University, Institute for Theoretical Physics, P.O. Box 105760, 69047 Heidelberg, Germany*; A. Kovac,* European Commission, Joint Research Centre Karlsruhe, P.O. Box 2340, 76125 Karlsruhe, Germany

In recent years the use of radiopharmaceuticals based on alpha-particle emitting radionuclides has seen a considerable growth. In pre-clinical research and first clinical trials targeted alpha therapy has shown great potential. However, there are still many challenges in this field, one being the need for tight chelating of the alpha-emitting radionuclides and their daughters. We aim to understand relations between bonding properties and bond stability of such compounds.

High-energy resolution X-ray absorption near edge structure (HR-XANES) spectroscopy is a valuable tool for the electronic structure study of actinides and lanthanides.[1-2] Here we employ it first to probe the bonding properties of La, a homolog of Ac, with different ligands in discussion as nuclide binding site in radiopharmaceuticals for targeted alpha treatment.

$[La(H_2O)_9]^{3+}$, $[La(TRIS)(H_2O)_6]^{3+}$, $[La(TRIS)_2(H_2O)^3]^{3+}$ (buffer media), $La(DOTA)(H_2O)]^{1-}$, $[La(MACROPA)]^{1+}$ and $[La(PSMA\text{-}617)(H_2O)]$ have been prepared and characterized. We measured La L_2-edge HR-XANES spectra at the Synchrotron Laboratory for Environmental Studies (SUL-X) beamline and La L_3-edge extended X-ray absorption fine structure spectroscopa (EXAFS) at the INE-Beamline at the KIT Light Source. Additionally, density functional theory (DFT) and FDMNES calculations were performed to compute the spectra. Bonding interactions were evaluated using natural orbitals for chemical valence (NOCV) and quantum theory of atoms in molecules (QTAIM) which describes the topology (i.e., shape and magnitude) of the electron density between two bonded atoms.

Several tools (spectroscopic and theoretical) to determine the covalency of the La-ligand bond were developed. One example of this measure can be the comparison of position and shape of the pre- and main absorption edges. EXAFS and HR-XANES analysis gave insights into the coordination environment. With QTAIM bond analysis the covalent from the ionic part of the bonding was differentiated. Combined these results are the first steps towards developing new spectroscopic tools that will help understand the electronic structure and the bonding and will potentially help designing new chelating ligands for use in radiopharmaceuticals for targeted alpha therapy.

References

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9:40am **TH1+AS+SS-TuM-6 Potential Energy Curves of Core-Excited States and Vibrational Broadening of X-Ray Adsorption Spectra of Uranyl*, Robert Polly,*** Karlsruhe Institute of Technology (KIT), Germany*; P. Bagus,* University of North Texas

It is well known that vibrational excitations lead to an observable broadening of the features in the X-Ray Photoelectron Spectroscopy, XPS, in ionic compounds. This broadening is described as a Franck-Condon, FC, broadening since it arises because there is a change in the equilibrium geometry of the ionized system from that in the initial, ground, state of the system. Studies have shown how the FC broadening is sensitive to coordination of the ionized atom [1] and to the covalent character of the cation – anion interaction [2]. For Uranyl UO_2^{2+} the different potential energy curves of the relevant core-excited states of the U $M_{4,5}$-edge manifold differ significantly and cause different broadenings for the three peaks which characterize the U $M_{4,5}$-edge X-Ray Adsorption Near Edge Spectroscopy, XANES. Thus, FC broadening effects affect the features as they do for XPS. This should be of particular importance in determining the resolution possible with High-Resolution XANES, HR-XANES [3-4]. However, to our knowledge, the possibility of different FC broadening in XANES or HR-XANES has not been considered previously and theoretical modeling of the spectra has used the same geometry for the initial and excited configurations [4-5]. In the present work, we examine vibrational excitations for the representative case of uranyl, UO_2^{2+}. The U $M_{4,5}$-edge HR-XANES spectra reveal three distinct peaks which are assigned to excitations into different 5f valence orbitals. The corresponding core-excited states differ significantly depending on the 5f valence orbital occupation and so does the FC broadening. Based on rigorous ab initio calculations of the wavefunctions, WFs, for the M_4 and M_5-edge XANES, we show that there are considerable changes in the geometry and we provide reliable estimates of the FC broadening due to these geometry changes. We also explain the linear behavior of the observed peak splittings with the internuclear distance, but we can not confirm a relation of the peak splittings with the covalence of the Uranium-Oxygen bond lengths.

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Theory for Surface Processes and Spectroscopies Focus Topic
Room B116 - Session TH2+AS+SS-TuM
Core-Level Spectroscopies II

Moderators: Ria Broer, University of Groningen, **Bianca Schacherl**, Karlsruhe Institute of Technology

11:00am **TH2+AS+SS-TuM-10 Cumulant Green's Function Approaches for Satellites and Multiplets in X-Ray Spectra*, John J. Rehr,*** Dept of Physics, University of Washington*; J. Kas,* Department of Physics, University of Washington **INVITED**

The treatment of electronic correlations in open-shell systems is one of the most challenging problems in atomic, molecular, and condensed matter physics. Their importance is particularly evident in x-ray spectra, where the single particle theory breaks down and many-body effects such as satellites and atomic multiplet effects are observed. Conventional approximations are only partly successful. Ligand-field multiplet theory and dynamical mean field theory can describe intra-atomic correlation effects well but typically ignore long range correlation effects. The real-time cumulant Green's function method can describe shake-up effects well [1] but ignores multiplets. We have found, however, that separating the dynamic Coulomb interactions into local and longer-range parts with *ab initio* parameters yields a combined multiplet-plus-cumulant approach that can account for both local atomic multiplets and satellite excitations [2]. The approach is illustrated for transition metal oxides and explains the multiplet peaks, charge-transfer satellites, and distributed background features observed in XPS experiment. In an alternative approach for molecular systems, we have found that a real-time equation of motion coupled-cluster (RT-EOM-CC) cumulant approach can also describe both correlation effects at the CCSD level and intrinsic losses in x-ray spectra, including orthogonality corrections that enhance XAS at the edge [3]. Comparisons with other approaches [4] are also discussed.

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[4] Analysis of the Fe 2p XPS for hematite Fe_2O_3: Consequences of covalent bondinand orbital splittings on multiplet splittings, P.S. Bagus, C. J. Nelin, C. R. Brundle, N. Lahiri, E. S. Ilton, and K. M. Rosso, J. Chem. Phys. **152**, 014704 (2020).

11:40am **TH2+AS+SS-TuM-12 Understanding Multiplets in the XPS of Transition Metal Oxides: Experiment and Theory and the Effects on Quantitation Procedures*, Christopher Richard Brundle,*** C. R. Brundle and Associates*; B. Christ,* XPS library*; P. Bagus,* Center for Advanced Scientific Computing and Modeling (CASCAM) Department of Chemistry University of North Texas **INVITED**

Atoms with open valence shells suffer splitting to their XPS core-levels owing to the different spin-spin coupling possibility between the remaining unpaired core electron and the electrons in the open shell (1). This results in a spectrum with two components of unequal intensity, separated by an ev or two. Gupta and Sen (2) expanded the multiplet splitting theory to include spin-orbit coupling (angular momentum coupling), providing highly cited predictions for the 2p spectra of TM cations (eg Ni^{2+}). Bagus, et al (3), and others, using rigorous ab initio MO calculations on clusters, have expanded theory further to allow XPS predictions for solid TM compounds (eg Ni^{2+} in NiO, Fe^{3+} in Fe_2O_3) which include both ligand field and bonding effects. Finally, they included shake-up effects (excitation of valence electrons in addition to core level ionization), which can substantially alter the distribution of intensities across the complete core-level spectrum, for example Ni 2p for NiO (4). This progression in the understanding of the origin of the features of TM core-level spectra is discussed, as is also the effects on requirements for providing quantitation of TM compounds using core level intensity ratios or peak fitting. Comparison is then made to alternative theory approaches to modeling the spectra, such as the freely available semi-empirical charge transfer method, CTM4XAS, (5), and the many-body cumulative theory of Rehr and Kass (6). We examine how these agree/differ in the interpretation/understanding of the XPS features, usefulness in ascribing chemical states, and quantitation aspects.

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Biomaterial Interfaces Division
Room B117-119 - Session BI+AS+EM+NS+SE+TF-TuA

Functional Biomaterials II: Sensing and Diagnostics

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

2:20pm **BI+AS+EM+NS+SE+TF-TuA-1 AVS Nellie Yeoh Whetten Awardee Talk: Detection of SARS-CoV-2 using Surface-enhanced Raman Spectroscopy and Deep Learning Algorithms***, **Yanjun Yang**[1],* University of Georgia*; H. Li,* Chongqing University, China*; L. Jones, J. Murray, D. Luo, X. Chen, H. Naikare, Y. Mosley, R. Tripp,* University of Georgia*; B. Ai,* Chongqing University, China*; Y. Zhao,* University of Georgia

A rapid and cost-effective method to detect the infection of SARS-CoV-2 is crucial in the fight against *COVID-19* pandemic. This study presents three strategies to detect SARS-CoV-2 from human nasopharyngeal swab (HNS) specimens using a surface-enhanced Raman spectroscopy (SERS) sensor with deep learning algorithms. The first strategy is to use DNA probes modified silver nanorod array (AgNR) substrate to capture SARS-CoV-2 RNA. SERS spectra of HNS specimens have been collected after RNA hybridization, and a recurrent neural network (RNN)-based deep learning (DL) model is developed to classify positive and negative specimens. The overall classification accuracy was determined to be 98.9%. For the blind test of 72 specimens, the RNN model gave 97.2% accuracy in the prediction of the positive specimens, and 100% accuracy for the negative specimens. The second strategy is to use a human angiotensin-converting enzyme 2 protein (ACE2) functionalized SERS sensor to capture the intact viruses. Such a method can differentiate different virus variants, including SARS-CoV-2, SARS-CoV-2 B1, and CoV-NL63. A convolutional neural network (CNN) deep learning model for classification and regression has been developed to simultaneously classify and quantify the coronavirus variants based on SERS spectra, achieving a differentiation accuracy of > 99%. Finally, a direct SARS-CoV-2 detection on SiO_2 coated AgNR substrate is tested. SERS spectra of HNS specimens from 120 positive and 120 negative specimens are collected. The HNS specimens can be accurately distinguished as positive or negative with an overall 98.5% accuracy using an RNN-based deep learning model, and the corresponding Ct value can be predicted accurately by a subsequent RNN regression model. In addition, 99.04% accuracy is achieved for blind SARS-CoV-2 diagnosis for 104 clinical specimens. All the detections are accomplished in 25 min. These results indicate that the SERS sensors combined with appropriate DL algorithms could serve as a potential rapid and reliable point-of-care virus infection diagnostic platform.

2:40pm **BI+AS+EM+NS+SE+TF-TuA-2 Wafer-Scale Metallic Nanotube Arrays: Fabrication and Application***, **Jinn P. Chu**,* National Taiwan University of Science and Technology, Taiwan

This presentation reports on the wafer-scale fabrication of metallic nanotube arrays (MeNTAs) with highly ordered periodicity. Various metals and alloys have been used to prepare MeNTAs via sputtering over a contact-hole array template created in the photoresist. We have used ferrous (stainless steel) and nonferrous (Cu-, Ni-, Al-, and Ti-based) alloys, as well as elemental metals (Cu, Ag, and Au), to form MeNTAs. The proposed nanotubes can be fabricated over a wide range of heights and diameters (from a few hundred nm to 20 µm) in various shapes, including tall cylinders and dishes. In addition, after combining with other nanomaterials (e.g., ZnO nanowires, graphene oxide, or Au nanoparticles), MeNTAs become nanohybrids suitable for many applications. These applications include thermal emitters, triboelectric nanogenerators, SERS-active biosensors, microfluidics, and anti-icing devices.

3:00pm **BI+AS+EM+NS+SE+TF-TuA-3 Low-Cost, Continuous Spectroscopic Monitoring of Chemical and Biological Contamination in Liquids***, **Liza White**, C. Howell,* University of Maine

Traditional UV-visible spectroscopic testing of liquids to assess contamination typically involves manual collection and measurement in a dedicated instrument at discreet time intervals. Here, we describe how low-cost, mass-produced diffraction gratings can be used to approach the functionality of traditional UV-visible spectroscopic readouts under continuous flow conditions. We designed and built a flow chamber setup that permitted uninterrupted monitoring of the diffraction pattern as water with different contaminants was passed over it. Various chemical dyes as well as biological contaminants such as bacteria and algae at varying concentrations in water were tested using standard LEDs as a light source. Information was extracted from the diffraction patterns by analyzing changes in the transmitted wavelengths as well as changes in scattering. Our results showed that the system permitted reasonable detection of each of the contaminants tested within a subset of the concentration range of a standard UV-vis instrument. Tests using the toxic dye methylene blue showed accurate detection well below the toxic limit (5 µg/mL), although the limit of detection for *E. coli* was higher at ~10^7 cells/mL. Our results demonstrate how mass-produced diffraction gratings can be used as low-cost detection systems for the continuous detection of contamination in liquids, opening the door for autonomous monitoring for a range of different applications.

3:20pm **BI+AS+EM+NS+SE+TF-TuA-4 Clickable Cerium Oxide Nanoparticles with Gadolinium Integration for Multimodal Micro- and Macroscopic Targeted Biomedical Imaging***, **Anna du Rietz**, C. Brommesson, K. Roberg, Z. Hu, K. Uvdal,* Linköping University, Sweden

Multimodal and easily modified nanoparticles enable targeted biomedical imaging at both the macro- and micro level. Computed tomography and magnetic resonance imaging are biomedical imaging techniques used daily in clinical practice all over the world. These non-invasive techniques can identify more medical conditions if contrast and sensitivity are increased. Commonly, targeted imaging is realized by conjugating biomolecular recognition elements such as antibodies to the contrast agent.

Herein, we present a clickable nanoparticle of our own design, consisting of a Cerium oxide nanoparticle core with integrated Gadolinium, coated with polyacrylic acid and functionalized with both a clickable moiety and a fluorophore. Click chemistry is a versatile toolbox of conjugation reactions that can be performed under gentle conditions enabling facile tailoring of the nanoparticles. Results from XRD and TEM studies clearly show that the cores are mono-crystalline and approximately 2 nm in diameter, the hydrodynamic radius of <5 nm is measured by DLS. The soft coat of the nanoparticles is characterized by IR spectroscopy as well as zeta potential measurements. We have verified the presence of azide-groups on the finished particles and the carboxylic groups of polyacrylic acid are firmly bound to the nanoparticle core. The nanoparticles have high colloidal stability even in physiological ionic strength environments with a zeta potential of -48 mV. We have proven direct anchoring of monoclonal antibody cetuximab to the nanoparticles enabling targeting of epidermal growth factor receptor, a common target in many cancer types. Fluorescence spectroscopy and relaxivity measurements were used to evaluate and optimize the properties for future imaging applications of tumors. The nanoparticles provide high MRI contrast with a T_1 relaxivity of 42 $s^{-1}mM^{-1}$ Gd, more than two times higher than currently used contrast agents. The finished antibody functionalized nanoparticles are efficiently purified using size exclusion chromatography, separating them from unbound nanoparticles and antibodies. Finally, the cellular uptake of the nanoparticles was evaluated using fluorescence microscopy as well as live/dead assays. We show that the nanoparticles are taken up by cell lines of head- and neck squamous cell carcinoma, in a lysosomal pattern. The nanoparticles are visualized at the nm scale inside the lysosomes using TEM. In conclusion, we have designed and synthesized a versatile nanoparticle with functionalized capping that enables facile fabrication of tailored nanoprobes for biomedical imaging.

4:20pm **BI+AS+EM+NS+SE+TF-TuA-7 Molecularly Imprinted Polymers (MIPs): Rising and Versatile Key Elements in Bioanalytics***, J. Völkle, A. Feldner,* Center for Electrochemical Surface Technology, Wiener Neustadt, Austria*; P. Lieberzeit,* University of Vienna, Faculty for Chemistry, Department of Physical Chemistry, Vienna, Austria*; **Philipp Fruhmann**,* Center for Electrochemical Surface Technology, Wiener Neustadt, Austria **INVITED**

Molecularly imprinted polymers (MIPs) are specific materials with tailored binding cavities complementary to a specific target molecule. Although the first example of artificial materials with molecular recognition were already described 80 years ago, they experienced a surge of popularity since the late 1990s due to improved synthetic methods and their great potential as recognition element in (biomimetic) sensors. MIPs can achieve similar selectivity and sensitivity as antibodies[1], while their robustness and stability is superior compared to biomolecules. They can also be used under non-physiological conditions, are suitable for long-term storage and accessed by scalable synthetic methods. These properties make them highly promising

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[1] **AVS Nellie Yeoh Whetten Awardee**

candidates for a wide range of applications, from biomimetic receptor layers to nanomaterials or artificial antibodies.

Despite this versatility, their design and optimization towards a specific analyte is probably the most challenging task in the development of a sensor. In general, MIP based sensors either rely on electrochemical, mass sensitive or optical transducers and are commonly used as thin film or nanoparticle (nanoMIP). While there is a considerable amount of literature on electrochemical sensors with MIPs available, new developments such as the improvement of conductive MIPs[2], optimized epitope imprinting[3], or the development of novel synthetic techniques such as the solid-phase synthesis of nanoMIPs[4] are highly important for the further development of MIPs in sensing.

For this reason, this presentation will provide an overview about different MIP types, their synthesis, application, and challenges. Furthermore, their potential in future applications with be addressed to give a wholistic impression of the numerous possibilities of this versatile compound class.

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#equal contribution

5:00pm **BI+AS+EM+NS+SE+TF-TuA-9 X-ray Fluorescence Analysis of Metal Containing Cytostatics in HeLa Cells using the Ultra-compact Cryo-vacuum Chamber µ-HORST**, ***Lejla Jusufagic**, C. Rumancev, A. Rosenhahn, A. Steinbrück, N. Metzler-Nolte,* Ruhr-University Bochum, Germany

Synchrotron-based X-ray fluorescence spectroscopy (XRF) is an excellent method for investigating elemental distributions and metal concentrations in biological systems.[1-4] The method provides a high sensitivity down to the detection of trace elements with high spatial resolution and penetration depth.[3,4] We introduced an ultra-compact cryogenic vacuum chamber called "µ-HORST" at the P06 nanoprobe beamline at PETRA III, DESY to measure 2D-XRF elemental distribution maps and concentrations in cryogenically fixated cells treated with cytostatic metal complexes with varying ligand sphere.[1,2] The cells are grown on silicon nitride membranes and treated with a 10 µM solution of the metal complexes for different durations and all physiological processes were stopped by rapid cryo-fixation. Cryogenic fixation is a non-destructive method that keeps the cells as close as possible to their biologically hydrated state. The frozen cell samples can be transferred into the µ-HORST setup and maintained in a frozen state throughout the nano-XRF measurements. The acquired data show that the concentration of the metal complexes and their intracellular location can be correlated to the one of physiologically relevant ions such as potassium and zinc as well as associated changes in the metal homeostasis. The developed chamber can not only be used for the analysis of intracellular cytostatic metal complexes, but also to the accumulation of antimicrobial metal complexes or of anthropogenic metals in environmental samples.

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5:20pm **BI+AS+EM+NS+SE+TF-TuA-10 Hemocompatibility Analysis of Novel Bioinspired Coating**, ***AnneMarie Hasbrook**, R. Faase, M. Hummel, J. Baio,* Oregon State University

Surface-induced thrombosis is a critical concern in medical device development. To minimize thrombosis, current extracorporeal circulation units require systemic anticoagulation. However, systemic anticoagulants can cause adverse effects such as thrombocytopenia, hypertriglyceridemia, and hyperkalemia. To address this issue, we combine the technology of polydopamine (PDA) functionalization with slippery liquid infused porous surfaces (SLIPS) to potentially enhance the biocompatibility of medical devices. PDA readily coats a wide variety of surfaces and can be functionalized with a thiolated fluoropolymer, via Michael Addition, to form a pseudo self-assembled monolayer (pSAM) which serves as the porous surface component of SLIPS. Liquid perfluorodecalin can then be added to complete the SLIPS coating. We hypothesized that the PDA SLIPS coating provides enhanced hemocompatibility due to its omniphobic properties and composition of compounds currently used in medical applications. Surface modifications were confirmed using contact angle and X-ray photoelectron spectroscopy (XPS) which revealed significant changes to the surface chemistry after the addition of each subsequent layer of PDA SLIPS. The coatings were evaluated for thrombogenicity via quantification of Factor XII (FXII) activation under static and dynamic settings, fibrin formation, platelet adhesion, and clot morphology. The PDA SLIPS coating activated 50% less FXII than glass and 100% more FXII than bovine serum albumin (BSA) coated substrates. PDA SLIPS had similar plasma clotting time to BSA and plasma clotted two times slower on PDA SLIPS than on glass. Platelet adhesion was increased two-fold on SLIPS compared to BSA and decreased two-fold on SLIPS compared to glass. PDA SLIPS had approximately 20% higher fiber diameter and 25% lower clot density than glass and was significantly different in fiber diameter and density than BSA.

5:40pm **BI+AS+EM+NS+SE+TF-TuA-11 Signal Enhancement for Gravimetric Biomimetic Detection – Conjugation of Molecularly Imprinted Polymer Nanoparticles to Metal Nanoparticles**, ***Julia Völkle**,* CEST GmbH, University of Vienna, Austria*; A. Weiß, P. Lieberzeit,* University of Vienna, Austria*; P. Fruhmann,* CEST GmbH, Austria

Over the past decades, the field of biosensors and -diagnostics has been increasingly dominated by a growing demand for non-centralized point-of-care devices that do not rely on extensive laboratory infrastructure and trained personnel. Recently, the COVID-19 pandemic has emphasized the crucial role of such fast, reliable, and affordable diagnostic tools. Novel, tailor-made nanomaterials are considered a key component for tackling the upcoming challenges of miniaturization and cost-efficiency in the field of biosensing.

One emerging class of such biomimetic nanomaterials are molecularly imprinted polymer nanoparticles (nanoMIPs). nanoMIPs are artificial receptors that can mimic the highly selective binding capabilities of biological recognition units, such as antibodies and enzymes. Unlike their natural counterparts however, they are stable under a wide range of non-physiological conditions, suitable for long-term storage, and can be derived from a straightforward, rapid synthesis procedure without the need for cell culturing or animal experimentation. Thus, they are ideal candidates for the development of sensitive, robust and inexpensive bioanalogous sensors.

While impressive results regarding their high selectivity and low non-specific binding have been reported [1], nanoMIP-based gravimetric (quartz crystal microbalance, QCM) assays are restricted with regards to the achievable limit of detection by their comparatively low overall mass. This project therefore is focused on the synthesis of well-defined nanoMIP-metal nanoparticle (NP) conjugates, which would result in a larger change in mass upon binding of the recognition units to the QCM transducer. Moreover, conjugation to gold-NPs would allow the incorporation of nanoMIPs into other analytical techniques such as lateral flow devices (LFDs). Experiments therefore are focused on the incorporation of suitable functional groups for further conjugation into the nanoMIP polymer network, the surface functionalization of metal NPs with complementary linker moieties and a suitable coupling procedure. In the poster, nanoMIPs selective for various biologically relevant species are coupled to metal NPs and the performance of the conjugates in QCM-based detection is presented in detail and discussed.

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Actinides and Rare Earths Focus Topic
Room C124 - Session AC+AS+TH-WeM

Nuclear Safeguards, Forensics, Environmental Science, and Stewardship

Moderators: Paul Roussel, AWE, **David Shuh**, Lawrence Berkeley National Laboratory, **Evgeniya Tereshina-Chitrova**, Charles University, Prague, Czech Republic

8:00am **AC+AS+TH-WeM-1 Simulation Tools for Improvement of the Fission Track Analysis Method for Nuclear Forensics***, **Itzhak Halevy,*** Nuclear Engineering, Ben Gurion Uni. Be'er Sheva, Israel **INVITED**

To answer nuclear forensics questions, we are developing new innovative techniques and approaches to make this analysis more reliable and accurate. Currently, only trained researchers can analyze microscope images. Since this analysis is dependent on the researcher's own abilities and skills, it is obvious that different researchers will produce results that are slightly distinct. A new worker's certification period is quite long, and it must cover numerous examples from previously measured data as well as some that we can only predict. A good simulation software can aid with training and provide a tool for grading new researchers.[1] The fission tracks were simulated by Monte-Carlo software, GEANT4, which uses all the physics behind the nuclear fission tracks, such as thermal neutrons flux, fission cross-section, radiation time, particle size, enrichment, etc. In this study, our Trainer2.0 software calculates the tracks on our Lexan detector and its projection, according to the physical parameters like neutron flax, size of the particle, the isotope, and radiation time. The result is a "star" centered on the simulated particle. Our full software is written with MatLab code.

We can simulate an extreme condition and learn new aspect in the fission track technique. From the simulation we can learn about the proper amount of material to use as a sample in the FTA technique.

The simulation can predict and compared to the mini-bulk and the micro-bulk analysis.

New idea of using penetrating fluorescent colors give as the ability to scan our detector in 3D instead of 2D. In this case we used the Dapi marker as a first shoot, this marker is well known for biomedical research.

This new idea to investigate the FT Star more than just by his projection.

Identifying the length of the tracks and their distribution allow us to determine the element source isotope be the shape of "fission products distribution" and the density of the impurities in the source.

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8:40am **AC+AS+TH-WeM-3 Characterizing Actinides in Subsurface Sediments for Contaminant Remediation***, **Carolyn Pearce**, H. Emerson,* Pacific Northwest National Laboratory*; C. Delegard,* TradeWind Services LLC **INVITED**

The nuclear weapons fuel cycle consists of front-end steps to produce, extract, purify, and engineer plutonium, and back-end steps to safely manage, prepare, and dispose of radioactive wastes. Waste processing has resulted in the release of actinides to the subsurface worldwide, including the release of ~200 kg of plutonium and ~7 Kg of americium from process waste solutions to unconfined soil structures at the Hanford Site in Washington State. The subsurface mobility of actinides is influenced by complex interactions with sediments, groundwater, and any co-contaminants within the waste stream. Developing efficient remediation strategies for released actinides requires a complete understanding of retardation processes and mass flux, including the different mechanisms by which actinides are immobilized in the subsurface, and the effect of localized subsurface conditions. Here, sediments from Hanford waste disposal sites have been selected, based on historical information and sediment composition, for characterization of actinide (plutonium, americium, and uranium) immobilization mechanisms. Results show that the actinides are present in these samples as micron-sized particles, intrinsic and pseudo-colloids, and dissolved species, and that they have been significantly affected by the chemistry of the actinide-bearing waste source term. Spectroscopic characterization of actinides has also proved essential to understand their migration in the deep, unsaturated, vadose zone sediments at the Hanford Site, due to the significant variability in solubility and mobility with speciation and oxidation state.

9:20am **AC+AS+TH-WeM-5 Changes in Oxidation Mechanism with Relative Humidity: Application to Uranium Dioxide Powders***, **Scott Donald**, L. Davisson,* Lawrence Livermore National Laboratory **INVITED**

It is of interest in nuclear forensic science to understand the relationship between an interdicted sample's history and the resulting chemical and physical characteristics.It may be possible to glean information on the environmental characteristics experienced by uranium dioxide from variations in the chemistry and structure of a powder sample.The reaction between high purity, stoichiometric UO_2 powder over a range of nominal conditions at room temperature was studied using a rage of techniques, including XPS, SEM, and TEM, to interrogate changes to both the surface and bulk properties of the material.Oxidation resulting from the interaction of the surface with the local environment was observed and quantified. A change in the reaction mechanism between low and high relative humidity has been proposed to describe the observed results.

The work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 and funded by the Office of Defense Nuclear Nonproliferation Research and Development within the U.S. Department of Energy's National Nuclear Security Administration.LLNL-ABS-848427

11:00am **AC+AS+TH-WeM-10 Spatially Resolved Morphological and Chemical Analysis of Nuclear Materials***, **Brandon Chung**, A. Baker, S. Donald, T. Li, R. Lim, U. Mehta, D. Rosas, S. Sen-Britain, D. Servando-Williams, N. Cicchetti,* Lawrence Livermore National Laboratory*; A. Ditter, D. Shuh,* Lawrence Berkeley National Laboratory (LBNL)

Nuclear forensics requires accurate identification of distinguishing material characteristics of interdicted nuclear materials. Local morphological and chemical variations in nuclear materials are nearly ubiquitous due to the varying provenance, process, and pathways. We will describe our efforts to strengthen operational and scientific methodologies to employ the focused ion beam-scanning electron microscopy (FIB-SEM) on uranium (U) and plutonium (Pu) materials for direct three-dimensional (3D) morphological analysis or to prepare site-specific material features to obtain spatially resolved characterizations using transmission electron microscopy (TEM) and X-ray synchrotron spectromicroscopy. Both U and Pu materials show variations in the internal chemical composition and morphology from their production processes and storage environments. This information is of potential use in discriminating material signatures to identify the origin and history of interdicted nuclear materials

11:20am **AC+AS+TH-WeM-11 Soft and Tender Spectromicroscopy for Nuclear Forensics at the Advanced Light Source***, **David Shuh**, A. Ditter,* Lawrence Berkeley National Laboratory (LBNL)*; N. Cicchetti,* University of Nevada Las Vegas*; R. Lim, S. Sen-Britain, D. Rosas, D. Servando-Williams, A. Baker, S. Donald, B. Chung,* Lawrence Livermore National Laboratory

The development of new methods and signatures is crucial to ensure that nuclear forensics activities remain effective. Synchrotron radiation analysis offers one way to extend the scope of forensics investigations in elemental, chemical, and structural analysis which all can be done in imaging modes that in some cases, reaches to the nanoscale. X-ray techniques are particularly useful because of their elemental specificity and non-destructive nature. The ability to use tunable, focused beams makes synchrotron radiation sources a potentially key tool for addition into the array of characterization techniques currently employed, particularly when it comes to the investigation of particles or areas of interest in smaller specimens. Recent efforts at the Advanced Light Source conducting tender and soft spectromicroscopy using x-ray fluorescence (XRF; Beamline 10.3.2) and a scanning transmission x-ray microscope (STXM; Beamline 11.0.2). The XRF measurements provide elemental analysis at the micron scale, whereas the STXM can probe chemical speciation with a spatial resolution of better than 25 nm. Several uranium and plutonium specimens have been investigated using these techniques and the potential signatures from this data, as well as its utility, will be demonstrated. The outlook for synchrotron radiation within nuclear forensics including the strengths and drawbacks of these techniques will also be discussed.

Applied Surface Science Division
Room B117-119 - Session AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM

Multi-Modal & Multi-Dimensional Analysis

Moderators: Gustavo Trindade, National Physical Laboratory, UK, **Paul Mack**, Thermo Fisher Scientific, UK, **Tim Nunney**, Thermo Fisher Scientific, UK

8:00am **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-1 Growth and Characterization of Large-Area 2D Materials***, **Glenn Jernigan,*** US Naval Research Laboratory **INVITED**

Nothing could be more coupled than Growth and Characterization. When two dimensional (2D) materials appeared on the radar of the scientific community (with the amazing properties of graphene), it was immediately obvious that large area samples would be needed. Exfoliating flakes was insufficient for the demands of scientific studies, in addition to not being viable should a commercial application be developed. Thus, the search began for growth methods to produce large-area 2D materials for large scale testing and development.

The Naval Research Laboratory has, over the past 15 years, pursued research programs in producing large areas of graphene, transition metal dichalcogenides (TMDs), boron nitride (BN), and other 2D materials. In every one of those programs, they began with surface analysis of composition, chemistry, and morphology of the grown films. The uniquely sensitive nature of x-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) and scanning tunneling and atomic force microscopy (STM and AFM) to 2D materials was necessary to measure the electrical, chemical, and physical properties obtained in the large area films and to understand what was observed in the exfoliated flakes. The production of large areas allowed "mass-scale" optical and electrical characterization, which then became a feedback loop in the search for new and interesting properties and relevant applications. In this presentation, I will show how we developed large-area graphene, by both epitaxial growth and chemical vapor deposition methods, TMDs, and other 2D materials for characterization and device utilization.

8:40am **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-3 Using a Correlative Approach with XPS & SEM to Measure Functionalized Fabrics for Antimicrobial Applications***, **Tim Nunney,** H. Tseng,* Thermo Fisher Scientific, UK*; D. Marković, M. Radetić,* University of Belgrade, Serbia

Medical textiles are an indispensable component for a wide range of hygienic and healthcare products, such as disposable surgical gowns and masks, or personal protection equipment, with opportunities to provide further protection by engineering textiles with suitable medical finishing. While antibiotics are considered a viable option for their efficiency in treating bacterial infections, their abuse can result in adverse effects, e.g., bacteria resistance. Nanocomposites have emerged as a promising alternative to antibiotics, as the large surface-to-volume ratio and high activity helps attain the targeted antimicrobial efficiency by using tiny amounts of nanocomposites, and their biocompatibility and scalability are particularly advantageous for medical applications [1]. Thus, developing processing methods to integrate nanocomposites in the fabrics is essential for exploiting their properties for medical textiles.

In this study, polypropylene fabrics, alginate and copper oxides, were selected to develop novel antimicrobial nanocomposites based on various surface treatments, i.e. corona discharge and alginate impregnation, which led to improved fabrics hydrophilicity with functional groups introduced as binding sites for Cu(II), a precursor that formed Cu nanoparticles when reacted with reducing agents, i.e. NaBH4 and ascorbic acid. The composition of the fabrics after being treated with corona discharge and impregnation observed by XPS indicates the materials formed mainly consisted of C and O, attributed to the presence of a thin, hydrophilic layer and alginate, respectively, consistent with depth profiling measurements. Following Cu reduction, XPS mapping of the fabrics finds that, reacting with ascorbic acid resulted in formation of nanocomposites containing a mixture of Cu and Cu (II) oxides across the surface, which could be visualised by using SEM in the same locations. Excellent anti-microbial activity against Gram-negative bacteria E. coli, Grampositive bacteria S. aureus and yeast C. albicans was observed for the treated fabrics[2]. This result not only demonstrates a cleaner, and healthier approach for developing novel nanocomposites, but more importantly highlights the role of surface techniques in uncovering challenges in designing and engineering functional textiles.

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[2] D. Marković, H.-H. Tseng, T. Nunney, M. Radoičić, T. Ilic-Tomic, M. Radetić, Appl. Surf. Sci., 527, 146829, (2020)

9:00am **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-4 Multi-Modal Analysis in Photoelectron Spectroscopy: From High-Resolution Imaging to Operando Experiments***, **Olivier Renault,*** CEA-Leti, France*; A. Benayad,* CEA, France*; N. Gauthier,* CEA-Leti, France*; R. Charvier,* ST Microelectronics, France*; E. Martinez,* CEA-Leti, France

Over the past years, the field of surface and interface analysis has been greatly expanded by new developments made possible by lab-scale instruments enabling higher excitation energies. These new developments are directly serving technological advances especially in the area of technologies in renewable energies and nanoelectronics, which are adressing more and more complex system requiring to go beyond traditional ways of characterizing surfaces and interfaces. Different dimensions are to be explored in multi-modal surface analysis : the depth dimension, the lateral dimension, and the dynamic dimension.

After a short review of some of the achievements towards enhancing the depth dimension by lab-scale hard X-ray photoelectron spectroscopy (HAXPES) and the lateral dimension using X-ray PEEM, we will present different application cases of *operando* HAXPES. Here, the material is analyzed as being part of a device operated *in situ* during the experiment, in conditions that are as close as possible to the final applications and where the interfaces can be studied in dynamic conditions. We will first review some results of *operando* HAXPES on resistive memories obtained with synchrotron radiation [1, 2] before presenting various lab-scale experiments [3, 4] and the current limitations to such approaches.

[1]B. Meunier, E. Martinez, O. Renault et al. *J. Appl. Phys*. **126**, 225302 (2019).

[2]B. Meunier, E. Martinez, O. Renault et al., *ACS Appl. Electron. Mater*. **3** (12), 5555–5562 (2021).

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[4]A. Benayad et al., *J. Phys. Chem. A* 2021, 125, 4, 1069-81.

9:20am **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-5 Multi-Modal Analyses of Ultrasonic-Spray-Deposited Ultrathin Organic Bathocuproine Films***, J. Chen,* ***Juliet Risner-Jamtgaard,*** *T. Colburn, A. Vailionis, A. Barnum, M. Golding,* Stanford University*; K. Artyushkova,* Physical Electronics*; R. Dauskardt,* Stanford University

Bathocuproine (BCP) is a small organic molecule that is typically used as an ultrathin hole blocking interlayer (< 10 nm thickness) in organic solar cells and perovskite solar cells. The film is typically deposited via low-throughput vacuum thermal evaporation with an *in-situ* Quartz Crystal Monitor to measure film thickness. Open-air ultrasonic spray deposition for low-cost and large-scale deposition is an attractive alternative method for solution processing of BCP films, but the process lacks a comparable *in-situ* metrology. Given that the BCP film is transparent to visible light and ultrathin, it is important to utilize a multi-modal approach to evaluate optoelectronic and physical properties of the sprayed film.

A suite of characterization techniques that span a range of equipment complexity, measurement time, and measurement sensitivity are used to analyze the BCP films. We begin by demonstrating the limitations of the singular ellipsometry model[1] for BCP found in literature and motivate a need to rely on other techniques. Multi-modal analyses including X-Ray Reflectivity, Angle-Resolved X-ray Photon Spectroscopy (AR-XPS), Auger Spectroscopy, Scanning Electron Microscopy, and Transmission Electron Microscopy with EELS are then performed on the sprayed BCP film. The advantages and disadvantages of each characterization technique are compared and discussed. We conclude that AR-XPS provides the most distinctive determination of individual layer thicknesses for a sample architecture consisting of silicon substrate/native SiO_x/BCP across the applicable range of AR-XPS from ~ 1-10 nm.

[1] Liu, Z.T., *et al*. The characterization of the optical functions of BCP and CBP thin films by spectroscopic ellipsometry. *Synthetic Materials*. 150(2):159-163. (2005)

9:40am **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-6 Combinatorial Synthesis and High-Throughput Characterization of Pt-Au Thin Films Fabricated by Confocal Magnetron Sputter Deposition***, **David Adams**, R. Kothari, M. Kalaswad, C. Sobczak, J. Custer, S. Addamane, M. Jain, E. Fowler, F. DelRio, M. Rodriguez, R. Dingreville, B. Boyce,* Sandia National Laboratories

A few binary metal alloys are predicted to form thermally stable, compositionally segregated structures owing to the thermodynamic preference for minority species to collect and remain at grain boundaries established within the solid.(J.R. Trelewicz et al., PRB, 2009) When produced as a nanocrystalline thin film, these stable structures afford the potential to maintain excellent mechanical properties (e.g., high hardness) even after annealing to elevated temperature. Indeed, several systems, including $Pt_{.9}Au_{.1}$ thin films, are reported to develop thermally-stabilized, hard, nanocrystalline structures attributed to solute segregation at grain boundaries.(P. Lu et al., Materialia, 2019)

Future studies that seek optimal stoichiometry and/or preferred synthesis processes require access to a wide range of composition as well as an ability to vary key deposition parameters. Toward this end, our team reports on the challenges and the benefits of combinatorial synthesis for expediting the discovery of improved binary metal thin films. Our study utilized confocal sputter deposition wherein Pt and Au targets were individually sputtered via pulsed DC magnetron methods. Substrates (150 mm diameter wafers) were fixed in order to gain access to a wide compositional range for each deposition. The sputter power and cathode tilt orientation were then varied in subsequent depositions to access the nearly full binary metal compositional range. The binary collision Monte Carlo program SiMTra (D. Depla et al., Thin Solid Films 2012), which simulates the transport of sputtered atoms within the process gas, helped guide the selection of these process parameters in order to achieve compositional goals in relatively few depositions. Notably, the binary compositions predicted by SiMTra closely matched (within a few molar %) the measured compositions determined by Wavelength Dispersive Spectroscopy completed in 112 different areas across each wafer. The various combinatorial Pt-Au films were further characterized by high-throughput Atomic Force Microscopy, automated X-ray Diffraction, fast X-ray Reflectivity, mapping four-point probe sheet resistance, and automated nanoindentation. These studies reveal how hardness, modulus, film density, crystal texture, and resistivity of combinatorial films varied with composition as well the atomistics of film deposition. Attempts to correlate key film characteristics with the kinetic energies and incident angles of arriving metal species (estimated by SiMTra) are discussed with a goal of improving fabrication processes.

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11:00am **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-10 Optical and X-Ray Characterization and Metrology of Si/Si(1-X)Ge(X) Nanoscale Superlattice Film Stacks and Structures***, **Alain Diebold**,* SUNY Polytechnic Institute **INVITED**

As traditional scaling of transistors comes to end, transistor channels and capacitors are being stacked to form new 3D transistor and memory devices.Many of these devices are fabricated using films stacks consisting of multiple Si/Si(1-x)Gex layers known as superlattices which must be fabricated with near atomic precision.In this talk, we discuss how Optical and X-Ray methods are used to measure the feature shape and dimensions of these structures.The use of X-Ray methods such as ω-2θscans and reciprocal space maps provide layer thickness and stress characterization. We will use simulations to show how a buried layer with a different thickness or Ge concentration alters the data. Recent electron microscopy studies have quantified the stress at the interfaces of these superlattices.We will also discuss how Mueller Matrix spectroscopic ellipsometry (MMSE) based scatterometry is used to measure feature shape and dimension for the nanowire/nanosheet structures used to fabricate nanosheet transistors and eventually 3D DRAM.The starting point for optical scatterometry is determining the optical properties of stressed pseudomorphic Si(1-x)Gex.MMSE can be extended into the infra-red and into the EUV.In addition, small angle X-Ray scattering has been adapted into a method knows as CDSAXS which can be used to characterize these structures.This talk will be an overview of these methods.

11:40am **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-12 Non-Destructive Depth Differentiated Analysis of Surfaces Using Ion Scattering Spectroscopy (ISS), XPS and HAXPES***, **Paul Mack**,* Thermo Fisher Scientific, UK

Recently there has been renewed interest in probing deeper into surfaces using HAXPES in addition to the more surface sensitive (soft X-ray) XPS. On modern XPS systems, with high sensitivity, the total sampling depth may be somewhere between 10nm and 15nm but HAXPES enables the analyst to look deeper, without having to destructively sputter the surface with ions. For a complementary, more comprehensive analysis, XPS and HAXPES can be combined with Ion Scattering Spectroscopy (ISS). ISS is far more surface sensitive than XPS, typically being thought of as a technique to analyse the top monolayer of a sample for elemental information.

In this work, the combination of XPS, HAXPES and ISS on a single tool has been used to give a non-destructive depth differentiated analysis of a range of samples, including a perovskite and an industrially relevant material containing multiple transition metals. The combination of all three techniques provides insight into the depth distributions of elements and chemical states, from the top monolayer to beyond 20nm into the surface.

12:00pm **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-13 Towards Measurement of Molecular Shapes Using OrbiSIMS***, **Gustavo F. Trindade**, J. Vorng, A. Eyres, I. Gilmore,* National Physical Laboratory, UK

An OrbiSIMS [1] instrument features a dual analyser configuration with a time-of-flight (ToF) mass spectrometer (MS) and an Orbitrap^{TM} MS, which confer advantages of speed and high-performance mass spectrometry, respectively. The ability to combine the MS performance usually found in a state-of-the-art proteomics and metabolomics MS with 3D imaging at the microscale and from nanolayers of <10 nm of material has proved popular in a broad field of application from organic electronics to drug discovery. For secondary ions to be efficiently transferred to the Orbitrap analyser, the sample is biased by a target voltage V_T necessary to match the acceptance window of the Orbitrap. Furthermore, the ions kinetic energy from the SIMS collision process must be reduced. Therefore, in the OrbiSIMS, a transfer system with helium gas at a pressure P_{He} slows the ions and reduces their kinetic energy distribution through inelastic collisions with gas atoms. Usually, an Orbitrap is used with an ambient pressure ion source and so here an extra gas flow of nitrogen is introduced that leads to an increase of pressure P_{N2} to compensate.

We conducted a systematic assessment of V_T and P_{He} and P_{N2} on the transmitted secondary ion intensities [2] and revealed a complex behaviour, indicating the possibility for additional separation of ions based on their shape, stability, and kinetics of formation. We showed that the V_T for maximum transmission of secondary ions will not be the same for all molecules of the same material and that sometimes multiple maxima exist. Here, we present recent progress towards the understanding of these phenomena and how we are leveraging it to measure molecular shape by using reference trisaccharides raffinose, maltrosiose and melozitose [3].

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[3] G.F. Trindade *et al.*, In preparation.

Surface Science Division
Room D136 - Session SS+2D+AS+HC-WeM

Surface Science of 2D Materials

Moderators: Irene Groot, Leiden University, The Netherlands, **Bo-Hong Liu**, National Synchrotron Radiation Research Center

8:00am **SS+2D+AS+HC-WeM-1 Heterogeneous Photocatalysis: Alcohols on Bare and Metal-loaded TiO_2(110) and Fe_2O_3(012)***, **Moritz Eder**,* TU Wien, Austria*; P. Petzoldt, M. Tschurl,* Technical University of Munich, Germany*; J. Pavelec, M. Schmid, U. Diebold,* TU Wien, Austria*; U. Heiz,* Technical University of Munich, Germany*; G. Parkinson,* TU Wien, Austria

We investigated the (photo)chemistry of alcohols on TiO_2(110) and Fe_2O_3(012) in ultra-high vacuum. Our studies focused on the role of the metal co-catalyst in the photocatalytic reaction by comparing the reactivity of bare and metal-loaded surfaces. We show that photocatalytic reactions are not merely a couple of redox reactions, but an interplay of thermal and photon-driven surface reactions.

Our results demonstrated that the co-catalyst plays a crucial role in the outcome of the reaction. On TiO_2(110), alcohols are oxidized to the aldehyde/ketone and hydrogen surface species upon illumination. The hydrogen surface species were thermally converted to H_2 by the co-catalyst, allowing for a steady-state photocatalytic conversion of alcohols and the continuous production of molecular hydrogen. Using mass spectrometry, we determined turnover frequencies and rate constants. The identification of surface mechanisms on Fe_2O_3 is less advanced, but there seem to be strong parallels in the photochemistry.

Our studies shed light on the fundamental processes involved in photocatalytic reactions on metal-loaded surfaces and contribute to the development of sustainable energy technologies.

8:20am **SS+2D+AS+HC-WeM-2 Factors Governing the Reactivities of Transition Metal Carbides at Vapor/Solid and Liquid/Solid Interfaces***, S. Alhowity, A. Ganesan, M. Gharaee, O. Omolere,* ***Qasim Adesope****, K. Balogun, P. Chukwunenye, F. D'Souza, T. Cundari, J. Kelber,* University of North Texas

Transition metal carbides are of broad interest for both heterogeneous and electro-catalysis. However, fundamental understanding of chemical factors governing reactivities and selectivities at the vapor/solid and liquid/solid interfaces remain sparse. Herein, *in situ* XPS results, electrochemical measurements, and DFT-based calculations are presented regarding the reactivities of NbC and TaC in the presence of O_2 vapor, and reactivity in solution towards the reduction of N_2 to NH_3. NbC and TaC films were prepared by DC magnetron sputtering deposition, then exposed to O_2 vapor at room temperature, and analyzed by *in situ* XPS without exposure to ambient. Similarly prepared samples were also analyzed by *ex situ* XRD. These data show that, although Nb and Ta have similar oxophilicities, (a) deposited NbC films contain significant amounts of Nb oxide phases throughout the film, whereas TaC films deposited under similar conditions do not, and (b) the exposure of NbC films to O_2 at 300 K results in significant Nb oxide formation, but that TaC films remain inert towards O_2 under these conditions. DFT calculations indicate that this significant reactivity difference towards O_2 is due in large part to the greater Ta-C bond strength compared to Nb-C, and in part due to the relative energetic stabilities of the corresponding oxides. Electrochemical studies show that ambient-exposed NbC, with a Nb_2O_5 surface layer, becomes reactive towards N_2 reduction to NH_3 under acidic conditions, but only after etching in NaOH to remove the surface oxide layer. Additionally, chronoamperometric data indicate that this reactive NbC surface is eventually modified under electrochemical conditions and becomes relatively inert towards N_2 reduction with time. Experiments involving *in situ* sample transfer between UHV and electrochemistry environments demonstrate that electrochemically active NbC surfaces in solution comprise Nb sub-oxide surface layers, in line with previous studies showing that effective NRR catalysts contain surface transition metal ions in intermediate oxidation states, supporting both N_2 lone pair attraction and pi-backbonding to bind and activate the NN triple bond.

Acknowledgement This work was supported in part by the UNT College of Science through COS grants 1600089 and RSG-2023-002 and and in part by the NSF under grant no. DMR 2112864.

8:40am **SS+2D+AS+HC-WeM-3 Tunable Interfacial Electrochemistry at Moiré Material Interfaces***,* ***D. Kwabena Bediako****,* University of California at Berkeley **INVITED**

At electrode–electrolyte interfaces, crystallographic defects are frequently implicated as active sites that mediate interfacial electron transfer (ET) by introducing high densities of localized electronic states (DOS). However, conventional defects can be challenging to deterministically synthesize and control at an atomic level, challenging the direct study of how electronic localization impacts interfacial reactivity. Azimuthal misalignment of atomically thin layers produces moiré superlattices and alters the electronic band structure, in a manner that is systematically dependent on the interlayer twist angle. Using van der Waals nanofabrication of two-dimensional heterostructures, scanning electrochemical cell microscopy measurements, and four-dimensional scanning transmission electron microscopy, we report a strong twist angle dependence of heterogeneous charge transfer kinetics at twisted bilayer and trilayer graphene electrodes with the greatest enhancement observed near the 'magic angles'. These effects are driven by the angle-dependent engineering of moiré flat bands that dictate the electron transfer processes with the solution-phase redox couple, and the structure of the relaxed moiré superlattice. Moiré superlattices therefore serve as an unparalleled platform for systematically interrogating and exploiting the dependence of interfacial ET on local electronic structure.

9:20am **SS+2D+AS+HC-WeM-5 Growth of Ultrathin Silica Films on Pt(111) and Rh(111): Influence of Intermixing with the Support***,* ***Matthias Krinninger****,* Technical University of Munich, Germany*; F. Kraushofer,* Technical University of Munich, Austria*; N. Refvik,* University of Alberta, Canada*; F. Esch,* Technical University of Munich, Germany*; B. Lechner,* Technical University of Munich, Austria

Silica is a widely used catalyst support material for clusters and nanoparticles. Understanding the relationship between these clusters and the support is challenging, however, because SiO_2 is insulating, and in most applications not crystalline which drastically limits the use of experimental techniques to those that work on insulating samples and are not diffraction-based. Several previous studies have investigated ultrathin, quasi-2D silica films on a variety of metal supports [1], which can then be measured by scanning tunneling microscopy (STM), XPS and most other surface science methods. Previous work on Pt(111) did not result in closed films, which was attributed to lattice mismatch [2]. We show that closed films can in fact be grown on Pt(111) when silica is deposited in excess, likely due to formation of a platinum silicide layer with slightly expanded lattice constant at the interface. We also report results of film growth on Rh(111), which is a near-perfect match to the lattice constant of freestanding SiO_2 films as calculated by theory. However, no high-quality films were achieved on Rh due to thermodynamic competition with a surface silicide.

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9:40am **SS+2D+AS+HC-WeM-6 CO_2 Adsorption on Graphitic-Like Bilayer ZnO Film Studied by NAP-XPS***,* ***Bo-Hong Liu****, S. Cheng,* National Synchrotron Radiation Research Center, Taiwan

CO_2 activation is a fundamental process in heterogeneous catalysis. ZnO-based catalyst has been extensively used in commercial methanol synthesis from CO_2 gas and the reverse water gas shift reaction. The adsorption behavior of CO_2 on the catalyst surface is pivotal to the reactivity. Whereas ZnO(0001)-Zn physisorbed or weakly chemisorbed CO_2,[1] strong chemisorption of the molecule happens on non-polar surfaces, such as ZnO(10-10), resulting in a tridentate carbonate.[2] In Operando TEM investigation during methanol synthesis shows that ZnO single atomic layer stacks distortedly around Cu nanoparticles via strong metal-support interaction. The lake of interlayer ordering between the layers suggests a weak interlayer interaction; therefore, each layer resembles a free-standing sheet.[3] DFT modeling concluded that free-standing ZnO(0001) layer adopts an graphitic-like co-planner structure. The co-planner feature was verified experimentally for the bi-layer ZnO(0001) supported on Ag(111) and Au(111).[4] On Au(111) substrate, TPD shows that CO_2 adsorbs on the low coordinate sites at the layer edges.[5] In the present study, we investigate the CO_2 adsorption on bi-layer ZnO/Ag(111) film using NAP-XPS to extend the pressure condition towards reality. We found a more considerable CO_2 chemisorption at elevated pressure. The presentation will also address how the surface hydroxyl group influences CO_2 adsorption.

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11:00am **SS+2D+AS+HC-WeM-10 Investigation of Nitride Spintronic and Kagome-Structured Intermetallic Topological Materials Using Molecular Beam Epitaxy and Scanning Tunneling Microscopy***, **Arthur R. Smith,*** Ohio University Physics and Astronomy Department

Owing to the overwhelming interest in topological [1] and spintronic materials [2], it is imperative to investigate these down to the atomic scale for their possible use in advanced devices. Many promising properties discovered among nitride materials, such as chemical stability and wide band gaps [3], may be combined with the equally promising aspects of topological materials, such as the topological Hall and Nernst effects [4]. Very recent work illustrates that spin-polarized scanning tunneling microscopy is a powerful tool for exploring topological band-structured Kagome antiferromagnets [5]. In our current work, we investigate both nitride material systems grown using molecular beam epitaxy as well as the growth of topological systems such as Kagome antiferromagnetic materials. Ongoing work in our group encompasses the investigation of Mn_3Sn, FeSn, CrSn, Mn_3Ga, and as a spintronic and topological nitride, Mn_3GaN. These materials are grown in combined UHV MBE and scanning tunneling microscopy chamber systems in which the grown samples are first fabricated using MBE and after that investigated for their structural, electronic, and magnetic properties including using STM and tunneling spectroscopy. Our goal is also to investigate these materials using spin-polarized STM as a function of temperature and applied magnetic field. Our current results show that these materials can be fabricated effectively using molecular beam epitaxy and investigated using various *in-situ* techniques such as reflection high energy electron diffraction and STM. Results from multiple on-going investigations will be presented with a birds-eye view of the progress. Especially to be presented will be STM and STS results in these Kagome systems grown using MBE.

This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE-FG02-06ER46317.

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11:20am **SS+2D+AS+HC-WeM-11 Molecular Beam Epitaxial Growth and Investigations of FeSn on $LaAlO_3$***, **Tyler Erickson**, S. Upadhyay, H. Hall, D. Ingram, S. Kaya, A. Smith,* Ohio University

Kagome antiferromagnetic and ferromagnetic materials provide an interesting avenue for research through the investigation of frustrated magnetism, band topology and electronic correlations [1-4]. FeSn is a layer-wise antiferromagnetic Kagome structured material with characteristic dispersion-less flat bands and Dirac cones at the Brillouin zone boundaries. Li *et al.* have presented exciting spin-polarized scanning tunneling microscopy results revealing surface electronic and magnetic properties of *in-situ* cleaved bulk FeSn [1]. Zhang *et al*. reported strain engineering of FeSn on $SrTiO_3$ (111) with precise control of the stanene layers [2]. Kawakami *et al.* reported Fe_3Sn_2 growth on Pt buffer layers on top of Al_2O_3 and studied various topological phenomena of this topological Kagome material [3,4]. Bhattarai et. al. studied the magnetotransport properties of FeSn grown on silicon substrates [5]. Here, we study the growth of FeSn directly on $LaAlO_3$ and report the successful growth of high-quality crystalline thin-films of FeSn. Reflection high-energy electron diffraction and x-ray diffraction are used to discover the *in-plane* and *out-of-plane* lattice constants, while atomic force microscopy and Rutherford backscattering provide topographical and stoichiometric characterization. Preliminary results indicate *in-plane* and *out-of-plane* lattice constants of 5.290 Å and 4.56 Å compared to the expected results of 5.297 Å and 4.481 Å, respectively. Besides discussing the thin film FeSn growth results, we also plan to present scanning tunneling microscopy results on the MBE-grown surfaces.

This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE-FG02-06ER46317.

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11:40am **SS+2D+AS+HC-WeM-12 AVS Graduate Research Awardee Talk: Molecular Beam Epitaxial Growth, Structural Properties, and Surface Studies of *a*-Plane-Oriented Mn_3Sn on *C*-Plane Al_2O_3***, **Sneha Upadhyay**[1], T. Erickson,* Ohio University*; J. Hernandez,* Universidad Autonoma de Puebla, Mexico*; H. Hall, K. Sun,* Ohio University*; G. Cocoletzi,* Universidad Autonoma de Puebla, Mexico*; N. Takeuchi,* Universidad Nacional Autonoma de Mexico, Mexico*; A. Smith,* Ohio University

Recently, Chen *et al.* reported the observation of tunneling magnetoresistance in an all-antiferromagnetic tunnel junction consisting of $Mn_3Sn/MgO/Mn_3Sn$.[1] Furthermore, Bangar *et al.* demonstrated a technique for engineering the spin Hall conductivity of Mn_3Sn films by changing the Mn: Sn composition.[2] These works show the potential of studying this Kagome antiferromagnetic material and the importance of being able to grow smooth films. This work uses molecular beam epitaxy to investigate the growth of Mn_3Sn ($11\underline{2}0$) on Al_2O_3 (0001). The growth is monitored *in-situ* using reflection high energy electron diffraction and measured *ex-situ* using X-ray diffraction, Rutherford backscattering, and atomic force microscopy.In our previous work, we carried out a single-step growth at 450°C, which resulted in a crystalline but discontiguous *a-plane-oriented* (~43% $11\underline{2}0$) Mn_3Sn film with a mix of other orientations including 0002.[3] Leading from this work, changes were made to the growth recipe, which involved carrying out a two-step growth procedure at room temperature, resulting in a contiguous, epitaxial Mn_3Sn film with up to ~82% $11\underline{2}0$-orientation. We are also exploring the effect of varying the Mn: Sn flux ratio and the film thicknesses (in the range of 5 – 200 nm) on the film crystallinity and orientation. We observe that varying the Mn: Sn flux ratio leads to a change in the RHEED patterns from pointy to streaky, and the XRD shows that the $11\underline{2}0$ peak can be varied between~ 82 % to ~38 % of all the peaks' total intensity. We also plan to present the first results on ultra-high vacuum scanning tunneling microscopy imaging of the ($11\text{-}\underline{2}0$) Mn_3Sn surface.

Acknowledgments:

The authors acknowledge support from the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE-FG02-06ER46317. The authors would like to thank Dr. Eric Stinaff and his students for back-coating the sapphire (0001) substrates.

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[1] **AVS Graduate Research Awardee**

Actinides and Rare Earths Focus Topic
Room C124 - Session AC+AS+MI+TH-WeA

Emerging Topics and Methods in Actinide/Rare Earth Sciences

Moderators: Edgar Buck, PNNL, **Krzysztof Gofryk**, Idaho National Laboratory, **Liane Moreau**, Washington State University

2:20pm **AC+AS+MI+TH-WeA-1 Chemical Imaging and Applications Using High Energy Resolution Fluorescence Detection for the Actinides***, **Samuel Webb**, N. Edwards, V. Noel,* SLAC National Accelerator Laboratory **INVITED**

Microscale synchrotron radiation-based x-ray fluorescence (SR-XRF) chemical analyses can provide a unique capability for chemical signature recognition and classification capabilities for actinide micro-particle analysis. SR-XRF is well suited to forensic type analyses of small particles because it is rapid, non-destructive, highly sensitive, has good spatial resolution, and can provide chemical information on the elements that are present when combined with x-ray absorption spectroscopy (XAS). The combination of spatially resolved distribution and chemical information, often known as chemical imaging, effectively provides a "chemical morphology" of the sample of interest and can show how chemical states are distributed within and among a series of particles. This type measurement is critical for understanding particle origin and history, as the spectroscopy, and its spatial distribution, can provide unique and complementary chemical signatures that may not be elucidated with other forms of measurement.

However, the conventional XAS capability in the near edge region as commonly implemented is often inadequate for systems that require high sensitivity or require a higher detail of spectroscopic information. This can be overcome with the combination of traditional micro SR-XRF and XAS, integrated with a high energy resolution fluorescence detector (HERFD) crystal analyzer. This has been recently implemented at BL 6-2b at SSRL and applied in the determination of the micron-scale oxidation state of uranium in particles. A discussion of the image and data processing techniques that can be applied using spatially resolved HERFD to obtain chemical and structural information, as well as the distribution of phases across different particles at the micro-scale, will also be presented.

3:00pm **AC+AS+MI+TH-WeA-3 High Energy X-Ray Characterization of Microstructure at Macroscopic Depths in Pu Alloys***, **Donald Brown**,* Los Alamos National Laboratory*; T. Carver, R. Pokharel,* los alamos National Laboratory*; A. Smith,* los al*; P. Kenesei, J. Park,* Argonne National Laboratory **INVITED**

High energy (95keV) X-rays were utilized to characterize the microstructure of six PuGa alloy samples. The samples had different gallium content, age, and history (i.e. thermos-mechanical processing). The crystallographic textures, phase fractions, lattice parameters and dislocation densities of each sample were evaluated through distinct analysis techniques. The textures of the samples were modest. In each case, the dislocation densities were relatively high, comparable to cold worked metals, with some attributable to mechanical work and some likely due to self-irradiation damage (aging). The lattice parameters determined in the predominantly single-phase samples were larger than expected based on the nominal Ga concentration. The lattice parameter increase is attributed to self-irradiation induced Ga segregation leaving the matrix Ga lean. Finally, measurements of the lattice parameter were completed as a function of temperature to determine the crystallographic thermal expansion of the material.

4:20pm **AC+AS+MI+TH-WeA-7 Native Oxide Growth of Pu—Ga Alloys***, **Kasey Hanson**, S. Hickam, D. Olive, A. Pugmire,* Los Alamos National Laboratory

Plutonium corrosion has proven to be an intricate area of research that garners considerable attention. In particular, understanding plutonium oxidation is significant to the safe handling and storage of plutonium metal, which is known to readily oxidize under ambient conditions. In order to mitigate this, plutonium metal is commonly stored in inert atmospheres. These include gloveboxes as well as ultra-high vacuum (UHV) chambers used for materials characterization. The objective of this work is to measure oxidation rates of plutonium metal in various storage environments. To achieve this, spectroscopic ellipsometry was selected due to its prevalence in a variety of industries to measure thin-film thickness.A non-destructive technique, ellipsometry exposes the sample to polarized light, and through changes in the amplitude ratio and phase difference of the reflected vs. incident light, one can generate a material's optical properties that can be used to determine oxide thicknesses.

Building upon previous work, this presentation will present the optical constants of plutonium metal, achieved through the use of ion sputtering under UHV, and plutonium oxide formed on plutonium metal in various storage and exposure conditions.These results will then be used to model oxide thickness values directly from ellipsometry measurements as well as provide additional insights into the nature of the oxide films relevant to plutonium storage and handling.

4:40pm **AC+AS+MI+TH-WeA-8 Molecular Beam Epitaxy of Ternary Nitrides: From Transition Metals to Actinoids***, **Kevin Vallejo**,* Idaho National Laboratory*; S. Gutierrez Ojeda,* Universidad Nacional Autonoma de Mexico*; G. Hernandez Cocoletzi,* Benemerita Universidad Autonoma de Puebla, Mexico*; S. Zhou, K. Gofryk, B. May,* Idaho National Laboratory

The exceptional properties of transition metal nitrides for coatings, as well as photo- and electrochemical applications have opened the doors for more detailed studies of their structure and synthesis. Mn- and Cr- nitrides are strong candidates to showcase the application of spintronic and magnetic sensing applications partially because of their ability to form several different metastable phases. Similarly, rare-earth nitrides have been studied for over 50 years due to their optical properties and strong electron correlations, leading to behaviors that range from insulating to metallic. This study uses molecular beam epitaxy to synthesize epitaxial thin films of different Mn-, Cr-, Ga-, and Ce-nitride phases. The electrical and magnetic properties of these films are investigated with the rocksalt MnN and CrN both showing metallic behavior, with the latter showing a magnetic transition ~280K. However, when combining these materials at similar growth conditions, instead of maintaining the rocksalt structure, a new ternary cubic phase of Mn_xCr_yN is obtained which shows narrow-gap semiconducting behavior. Additionally, density functional theory calculations show potential new phases where lanthanoid ternary phases are experimentally realizable. This work presents an avenue for the epitaxial integration of metallic, magnetic, and semiconductor materials via transition metal and lanthanoid compounds, en route to the synthesis of actinoid compounds.

5:00pm **AC+AS+MI+TH-WeA-9 Formation and Electronic Properties of Uranium Tellurides: A Thin Films Study***, **Evgenia Tereshina-Chitrova**, S. Alex,* Institute of Physics CAS, Prague, Czechia*; O. Koloskova, L. Horak,* Charles University, Prague, Czechia*; O. Romanyuk, Z. Soban,* Institute of Physics CAS, Prague, Czechia*; T. Gouder, F. Huber,* JRC Karlsruhe, Germany

Understanding the interaction of 5f electrons with other electrons in actinide compounds presents a significant challenge. Factors such as relativistic effects, strong electron correlations, and hybridization with ligands contribute to the complexity of observed effects. This complexity is exemplified in the case of the recently discovered unconventional superconductor UTe_2 [1]. The ongoing debate surrounding UTe_2 revolves around understanding its unconventional superconductivity, the nature of its electronic correlations [2,3], and the character of the 5f electrons. While it's evident that UTe_2 exhibits intermediate occupancy of the 5f states at ambient pressure, there are two opposing interpretations of experimental findings regarding the degree of localization of the 5f electrons: the model based on $5f^26d^1$ states with singlet crystal field states [4,5], and a $5f^3$-based model with atomic Kramers doublet and greater 5f itinerancy [6,7]. Interestingly enough, ab-initio calculations considering the $4f^2$ U-ion ground state multiplet reproduce bulk experimental observations, such as the Schottky anomaly and magnetic anisotropy at low temperatures [8].

To contribute to this subject, we provide a comprehensive and detailed investigation of thin films of uranium tellurides with various compositions U_xTe_y by means of X-ray Photoelectron Spectroscopy (XPS) and Ultra-violet Photoelectron Spectroscopy (UPS). We also explore the structural and bulk properties of the films, including their magnetic and transport characteristics. This comprehensive approach allows us to correlate the changes in XPS spectra across different compositions and crystal structures with resultant bulk properties, contributing to our understanding of the nature of the 5f electrons within uranium tellurides.

The work by E.A. T.-Ch. is supported by the Czech Science Foundation (GAČr) under the grant number 22-19416S. E.A. Ch.-T. is a recipient of the L'Oreal-UNESCO for Women in Science prize.

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5:20pm **AC+AS+MI+TH-WeA-10 Nanoscale Uranium and Thorium Oxides for Applications in Advanced Nuclear Fuels***, **Matthew Heaney**, L. Moreau, X. Guo,* Washington State University

Nanomaterials of uranium and thorium oxides and their mixtures are of significance to the development of advanced nuclear fuels with properties such as self-healing and greater fission gas retention. They also serve as a means for furthering our understanding of spent nuclear fuel behaviors. Furthermore, thorium incorporation into the uranium sublattice induces changes in oxidation behavior, which would be a promising means to provide additional redox resistance. Coupling this with the possible application in fast neutron reactors presents a potential fuel for the Th fuel cycle, which is inherently proliferation resistant. However, these possible applications are purely hypothetical given that, compared to nanomaterials from the rest of the periodic table, actinide nanomaterials are heavily understudied. Therefore, it will be imperative to interrogate the properties of these nanomaterials. This work aims to explore three key areas. (1) How careful kinetic control through variations in synthetic methods can be used to produce particles with different sizes, shapes, and heterogeneities of mixing. (2) Elucidation of the structural and thermodynamic properties of these nanomaterials and how characteristic size, shape, and heterogeneity of mixing affect them through a variety of X-ray characterization and calorimetry techniques. X-ray characterization techniques such as X-ray absorption spectroscopy (XAS) is used to evaluate the heterogeneity of mixing, local structure, and oxidation state of particles while small-angle X-ray scattering (SAXS) is used to determine statistical values on particle size, shape, and polydispersity. Calorimetry techniques like high temperature drop calorimetry are used to determine enthalpies of formation for nanoparticles and the contribution surface effects have on the thermodynamics or thermogravimetric analysis-differential scanning calorimetry (TGA-DSC), which can be used to evaluate oxidation behaviors. (3) How sintered nanoparticles behave in *in-situ* reactor conditions as nuclear fuels and how particle characteristics can be chosen to achieve more desirable radiation-resistance and thermal properties for nuclear fuel, through irradiation studies performed at the 1-MW TRIGA reactor on the campus of Washington State University. Overall, the work presented provides initial evidence for the benefits of nanomaterials in the production of advanced reactor fuels and outlines important fundamental properties of actinides on the nanoscale.

Applied Surface Science Division
Room B117-119 - Session AS+CA+EL+EM+SE+SS+TF-WeA

Quantitative Surface Analysis I

Moderators: David Cant, National Physical Laboratory, UK, **Peter Cumpson**, University of New South Wales, **Christopher Moffitt**, Kratos Analytical Inc, **Lev Gelb**, University of Texas at Dallas

2:20pm **AS+CA+EL+EM+SE+SS+TF-WeA-1 Status of Efforts to Upgrade the Quality of Surface Analysis Data in the Literature***, **Donald Baer**,* Pacific Northwest National Laboratory

Multiple efforts are being undertaken to address a growing presence of faultysurface analysis data and/or analyses appearing in the literature. Issues include bad data, incorrect analysis, and highly incomplete reporting of instrument and analysis parameters. This talk describes the status of four efforts to address some of the issues. Recognition of this problem within the surface analysis community has increased with an understanding that both inexperienced users and increased use of surface analysis methods outside the surface analysis community contribute to the problem. The current efforts build upon decades of development and efforts by standards committees, excellent books and journal publications, websites, short courses, and other efforts. A collection of guides, protocols and tutorials addressing reproducibility issues with a significant *focus on XPS* was published in JVSTA in 2020/21. A second collection, *Reproducibility Challenges and Solutions II,* with a more general focus on Surface and Interface Analysis was initiated in 2022 and is being finalized. The second collection addresses several techniques, including SIMS, SPM, and UPS, and includes topics such as theoretical modeling and machine learning in data analysis. A second effort focuses on a part of the community less interested in general understanding but needs to answer specific surface analysis questions. A new type of paper called Notes and Insights is being published in the journal Surface and Interface Analysis with the objective to provide incremental bits of useful information of importance to non-expert analysts. Two additional activities are underway to assist with reporting issues. Examination of papers in multiple journals found that instrument and analysis related information needed to assess or reproduce data is often incomplete or absent. To assist authors in reporting instrument parameters, papers describing in some detail related families of commercial instruments are being prepared for Surface Science Spectra. These papers describe the instrument, major components, geometry and provide example data related to common data collection modes. Authors will be able to reference these papers and identify specific modes of instrument operation used in their research. Another parameter reporting activity concerns sample handling before analysis. ISO Technical Committee 201 is developing a series of documents (ISO 20579 parts 1 to 4) on what needs to be reporting regarding sample handling, storage, processing, and mounting for analysis. These standards describe what needs to be reported and contain informative annexes that provide information regarding the needs and challenges to proper sample handling to produce reliable useful surface analysis data.

2:40pm **AS+CA+EL+EM+SE+SS+TF-WeA-2 The behavior of the Shirley background of the Ti 2*p* spectra across the Ti 1*s* edge***, **Dulce Maria Guzman Bucio,*** CINVESTAV-Unidad Queretaro, Mexico*; D. Cabrera German,* Universidad de Sonora, Mexico*; O. Cortazar Martinez, J. Raboño Borbolla,* CINVESTAV-Unidad Queretaro, Mexico*; M. Vazquez Lepe,* Universidad de Guadalajara, Mexico*; C. Weiland, J. Woicik,* National Institute of Standards and Technology*; A. Herrera Gomez,* CINVESTAV-Unidad Queretaro, Mexico

A wide variety of photoemission spectra display a step-shaped background, called the Shirley-type background, which should be accounted for in the total background signal for reliably assessing chemical composition. However, it cannot be modeled with any method based on extrinsic processes like the inelastic dispersion of the photoelectrons (e.g., Tougaard-type backgrounds). Although its physical origin is still unknown, experimental data suggest that the Shirley-type background is due to phenomena occurring inside the atom [1,2]. To gain insights into those phenomena, we studied the behavior of the Shirley-type background for the Ti 2*p* photoemission spectra.

In this work, Ti 2*p* photoemission spectra were acquired with Synchrotron light (at Beamline 7-2 at the Brookhaven National Laboratory) from a clean metallic titanium film (sputtered on a Si (100) substrate) capped with an ultra-thin aluminum layer. The spectra were collected with 44 excitation energies around the Ti 1*s* edge. By simultaneously fitting Ti 2*p* photoemission spectra obtained with excitation energies higher than the Ti 1*s* edge, we robustly determined the peak structure of the Ti 2p spectra. Outstandingly, the parameter of the Shirley-type background associated with the Ti 2*p* peak structure is modulated as the photon energy crosses the Ti 1*s* edge. The relation of this phenomenon with the physical origin of the Shirley background will be discussed. The $KVL_{2,3}$ Auger peaks—which overlap with the Ti 2*p* peaks—do not have a step-shaped background for most of the excitation energies.

Acknowledgments:

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3:00pm **AS+CA+EL+EM+SE+SS+TF-WeA-3 Chemical Analysis of Multilayer System by Photoemission: The Binding Energy Reference Challenge***, **Thierry Conard**, A. Vanleenhove,* IMEC Belgium*; D. Desta, H. Boyen,* University of Hasselt, Belgium

XPS is a well-established technique used for non-destructive analysis of the chemical composition of thin layers and interfaces. It is most commonly performed using Al Kα radiation (1486.6 eV), which limits the analysis to the top 5-10nm. The recently developed laboratory-based hard X-ray photoelectron spectroscopes (HAXPES) provide new analysis options. They enable the analysis of thicker film structures and interfaces buried down to 20-50 nm depending on the photon energy and facilitate the analysis of fragile buried layers without ion-induced chemical damage.

Increasing the number of analyzed (insulating) layers enhances the risk of significant vertical differential charging and makes the repeatability of binding energy determination more challenging. While charging has to be taken into account for XPS, the analysis of most XPS spectra is quite straightforward as long as the surface charge is stable and the lateral distribution of surface charge is uniform within the area of analysis. For HAXPES however vertical charge distribution comes into the game for a large group of structures whose development can benefit from HAXPES analysis. Vertical charge build-up can be complex, especially if examined structures exist of multiple layers and hence multiple interfaces, containing a large variety of materials. But even in 'simple' non-conducting one-layer structures a vertical charge gradient builds up when exposed to X-rays and small changes in the parameters of standard surface charge neutralization techniques - as the use of e-beam flood guns - can influence the nature of the charge gradient.

In this work, we will examine the influence of measurement conditions in single and multiple layers systems relevant to the microelectronic industry on the determination of precise binding energies.

HAXPES spectra of technologically relevant samples will be discussed to demonstrate the challenge of determining exact binding energy values. The set of examined samples comprises oxide layers Si samples and metal/high-k/Si stacks including high-k materials as HfO_2 and Al_2O_3. The surface potential will be precisely set and monitored in situ by depositing a metallic layer (such as Ag) on top of the stack and applying an external potential instead of using an electron neutralization source. All experiments are performed in a PHI *Quantes* system and/or a Scienta Omicron *HAXPES Lab*, both equipped with two monochromatic X-ray sources: an Al Kα (1486.6 eV) and a Cr Kα (5414.8 eV - *Quantes*) or Ga Kα (9252.1 eV – *HAXPES lab*) X-ray source.

3:20pm **AS+CA+EL+EM+SE+SS+TF-WeA-4 Where Are We on the Road-Map to Artificially Intelligent Interpretation of X-ray Photoelectron Spectra?***, C. Moffitt,* Kratos Analytical Inc*; A. Roberts, J. Counsell, C. Blomfield, **Kevin Good**, K. Macak,* Kratos Analytical Limited, UK

Robust peak identification is crucial for accurate sample analysis using X-ray photoemission spectroscopy (XPS). Automation of peak ID enhances this process by minimizing user error and bias. Current acquisition software offers improved computer-derived peak identification from unknown samples, instilling confidence in the correct identification of elements. Moreover, this forms the foundation for an automated sample analysis workflow known as Data-dependent Analysis (DDA). DDA involves identifying peaks in a survey spectrum and subsequently acquiring high-resolution spectra from major components. A recent User survey revealed that a significant majority of users rely on the large area survey acquisition mode as a starting point for analysis.

To provide a metric for confidence in the DDA process, existing spectral analysis data, which includes the element composition information, is used to generate reference spectra for testing purposes. These reference spectra serve as the basis dataset against which the performance of the automated analysis algorithm can be evaluated. By comparing the results of the algorithm with the reference spectra, statistical parameters can be calculated to assess the algorithm's precision, sensitivity, specificity, and accuracy in identifying elements of unknown spectra.

For experienced analysts, DDA serves as a time-saving acquisition method, while for inexperienced analysts, it provides assurance in accurate peak identification and appropriate high-resolution spectra acquisition. Here we highlight current status of automated XPS data acquisition in relationship to the 'expert system', championed in the early 2000's and full AI interpretation of XPS spectra of the future.

4:20pm **AS+CA+EL+EM+SE+SS+TF-WeA-7 Thin Film Analysis by XPS: Quantitative Analyses Using Physics-Based and Machine-Learning Approaches***, **Lev Gelb**, N. Castanheira, A. Walker,* University of Texas at Dallas

We present progress towards quantitative analysis of XPS data using both model-based "fitting" approaches and machine learning methods. Two separate applications are considered.

The first concerns the simultaneous extraction of both compositional profiles and sputtering parameters from XPS sputter depth-profiles of multilayer films. Depth-profile data are routinely processed to provide "fractional composition vs ion dose" profiles, but such analyses typically assume the sample is homogeneous in the probed region, which is not true near interfaces, and cannot precisely convert between units of ion dose and depth without extensive calibration data. Our approach is to first construct analytical models for both the sample structure and for the sputtering process, and then to determine the model parameters (layer thicknesses, interfacial widths, material removal rates, etc.) that are most likely given the observed apparent fractional composition profiles. This is done numerically, by iteratively comparing simulated and observed apparent composition profiles. The only additional required inputs are the inelastic mean free paths for each tracked peak in each material present. The efficacy of this approach is demonstrated using both synthetic and experimental data sets, and various model improvements (sputter-induced mixing, *in situ* chemical reactions) are discussed.

The second application concerns the application of machine-learning tools to remove the inelastic scattering background from XPS spectra in order that accurate peak areas can be obtained. Our approach here is to generate a training data set which consists of a thousands of simulated XPS spectra with and without inelastic scattering included. This is accomplished using the SESSA software package[1]. This data set is then used to train a neural network algorithm to output a "no-background" spectrum from an input "with-background" spectrum; this output spectrum can then be used to compute peak areas for compositional analysis. The training set generation methodology and network structure are discussed, and application of the tool to both simulated and experimental spectra is demonstrated.

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4:40pm **AS+CA+EL+EM+SE+SS+TF-WeA-8 Room Temperature Ionic Liquids as Reference Materials for Photoelectron Spectrometers***, **Benjamen Reed,*** National Physical Laboratory, U.K.*; J. Radnik,* BAM Berlin, Germany, UK*; A. Shard,* National Physical Laboratory, U.K.

Room-temperature ionic liquids (RTILs) are materials consisting of organic salts that are liquid below temperatures of 100°C and are used in several fields including electrochemistry,[1] pharmaceutics, and medicine.[2] RTILs have several notable properties that make them ideal for X-ray photoelectron spectroscopy (XPS) analysis. They have an extremely low vapor pressure and high surface tension, and so can be analysed using conventional XPS under ultrahigh vacuum without the need for near-ambient pressure instrumentation. Also, when deposited in a recessed sample holder, the meniscus of an RTIL will be perfectly flat meaning that there are no contributions from sample topographic effects. Finally, and most importantly, they are highly homogeneous and have well-defined stoichiometries.[3]

These properties make RTILs potential reference materials for validating the intensity calibration of a photoelectron spectrometer. RTILs with non-coordinating bistriflimide (NTf_2) anions (e.g. $PMIM^+NTf_2^-$) or dimethyl phosphate (DMP) anions (e.g. $MMIM^+DMP^-$) are such candidates, with core levels up to ~800 eV binding energy, making them apt for verifying the quantification of light elements, especially for organic materials.[4,5]

To accurately determine peak areas, however, requires the principal and secondary photoelectron signals to be deconvolved. Previous attempts by multiple laboratories using different quantification methods give a mean atomic composition within 1 at.% of the known stoichiometry, but some individual elements (such as fluorine) exhibit differences greater than 1 at.% because the elastic and inelastic secondaries are not suitably deconvolved. Attention must be paid to the energy loss function that defines the inelastic background over the full energy range of an XPS spectrum so that a suitable Tougaard background subtraction can be applied.[6] Here we present a study on several RTILs and discuss how they may be used to validate an XPS intensity calibration and provide confidence in measurements to XPS instrument operators.

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5:00pm **AS+CA+EL+EM+SE+SS+TF-WeA-9 Fractional Coverage Analysis of Monolayers with XPS and Non-Destructive Depth-Profiling with Combined Soft and Hard X-Rays***, **Norbert Biderman**, K. Artyushkova, D. Watson,* Physical Electronics USA

X-ray photoelectron spectroscopy (XPS) is a well-established technique for non-destructive analysis of the chemical composition of thin layers and interfaces. Angle-resolved XPS (AR-XPS) has been used to determine composition of depth profiles and layer thicknesses, traditionally with Al Kα (1486.6 eV) X-ray beams for depths up to 5-10 nm below the surface. In recent years, new AR-XPS capabilities have been added to Physical Electronics XPS scanning microprobe instruments including Cr Kα (5414.8 eV) hard X-ray photoelectron spectroscopy (HAXPES) that can probe buried interfaces up to 15-30 nm below the surface. Coinciding with the HAXPES development, the StrataPHI analysis software was developed to reconstruct quantitative, non-destructive XPS/HAXPES depth profiles from angle-dependent and single-angle photoelectron spectra.

In this talk, we will show that the StrataPHI software has been further developed to combine Al Kα and Cr Kα XPS and HAXPES data within a single depth profile to enhance extracted analytical information from various depths below the surface. We will explore the method of the combined technique as well as its application to multilayered thin film samples. The updated StrataPHI software also includes a fractional coverage analysis mode, relevant in situations where ultra-thin films exist as discrete islands – commonly observed in early thin-film deposition stages on the substrate rather than as a continuous, uniform film. A model system of discrete molybdenum sulfide (MoS2) monolayer triangles deposited on SiO2/Si substrate will be discussed.

Such added StrataPHI capabilities allow for scientists and engineers in metrology and research & development to analyze multi-layered thin films and ultra-thin films rapidly and non-destructively without potentially damaging ion beam sputtering that might otherwise be required to depth-profile or sputter-clean adventitious contamination off the surface.

5:20pm **AS+CA+EL+EM+SE+SS+TF-WeA-10 Reassessing the Reduction of Ceria in X-Ray Photoelectron Spectroscopy***, **David Morgan,*** Cardiff University, UK

Given its excellent redox abilities, the use of cerium dioxide (CeO_2, ceria) and related materials in catalysis is widespread [1]. This Ce^{3+}/Ce^{4+} redox shuffle allows for great catalytic ability and a method of correlation of catalytic activity to the state of ceria [2–4].Given that catalysis is a surface mediated process, XPS is critical in the analysis of pre- and post-mortem materials.

Over the years there has been debate on the degree of reduction of CeO_2 during XPS analysis. Therefore, in continuation of our work on understanding the reduction of materials in modern spectrometers [5], we have investigated different cerium oxide preparations and shown that not only is the rate of reduction dependent on instrument type and experimental configuration (and hence appropriate analysis protocols should be implemented), but is also related to the morphology of the cerium which may, at least in part, account for the discrepancies in the degree of reduction in the literature. It is postulated that reduction rates could be used to indicate likely ceria morphology where other analysis is unavailable.

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Acknowledgements

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5:40pm **AS+CA+EL+EM+SE+SS+TF-WeA-11 Using High Sensitivity – Low Energy Ion Scattering Spectroscopy (LEIS) to Unravel the Complex Nature of High Entropy Alloys***, **Matthias Kogler**, C. Pichler,* Centre for Electrochemistry and Surface Technology (CEST GmbH), Austria*; M. Valtiner,* Vienna University of Technology, Austria

Complex metallic materials such as Multi-Principal Alloys (MPEAs) and High Entropy Alloys (HEAs) have emerged as a promising class of materials given their unique inherent characteristics. Excellent mechanical, thermal, and corrosion properties allow for a broad spectrum of applications. However, due to the multi-element nature of these alloys, characterisation of the composition and microstructure proves to be a challenging task.

Especially with regard to corrosion-protective passivation films, the complex correlations with the corrosion behaviour are fully unclear to date, and require an in-depth atomic level characterisation and rationalisation. However, the precise layer by layer structure of such passive films is particularly demanding to assess, since traditional techniques such as XPS (X-ray photoelectron spectroscopy) or AES (Auger electron spectroscopy) have analysis penetration depths of several nanometres and cannot reach atomic layer resolution. However, to fully understand and quantify the passivation layer structure, such an atomic layer resolution of the surface region is necessary, due to the complexity of HEAs.

In order to obtain an exact understanding of the atomistic mechanism at the monoatomic layer level, High-Sensitivity - Low Energy Ion Scattering Spectroscopy (HS-LEIS), was applied, which provides the required monolayer sensitive resolution to study the passivation layers of such complex multi-component alloys. The unique surface sensitivity combined with the implementation of in-situ treatment methods enabled the real-time study of oxide layer growth, as well as the analysis of temperature-dependent changes in the elemental surface composition. Due to the high resolution achieved by static and dynamic sputter depth profile modes, we could determine the exact composition of the HEA passivation layer with resolution on atomic monolayer scale.

The findings provide the potential to significantly advance the current understanding of the passivation behaviour of MPEAs and HEAs, and the development of novel metallic materials with superior properties. Valuable insights for understanding the material characteristics for those highly advanced materials could thereby be generated.

Plasma Science and Technology Division
Room A106 - Session PS1+AS-WeA

Plasma Chemistry, Catalysis and Applications for the Environment and Sustainability

Moderators: Michael Gordon, University of California at Santa Barbara, **Kenji Ishikawa**, Nagoya University

2:20pm **PS1+AS-WeA-1 Synthesis of Hydrogen and Structural Carbon Materials from Methane Using Radiofrequency Nonequilibrium Plasma***, **Elijah Thimsen,*** Washington University in St. Louis **INVITED**

The production of hydrogen from methane by dehydrogenation of carbon is up to 6 times less energy intensive than water splitting and involves no intrinsic CO_2 byproduct. If hydrogen were used as a fuel at societal scale, billions of tons per year of carbon co-product would be produced. Steel and concrete are manufactured goods that are used at a scale of billions of tons per year, for structural applications. To avoid massive waste, the carbon co-product from hydrogen production could be used in structural applications, perhaps to displace concrete and steel. In this talk, I will focus on the use of radiofrequency capacitively coupled electrodeless discharges in a tubular flow-through configuration for methane dissociation. The plasma step of our process currently operates in the pressure range from 0.025 to 0.125 bar, and the goal is to synthesize an equimolar mixture of C_2H_2 + HCN from CH_4 + N_2. The mixture of C_2H_2 + HCN is an intermediate between the plasma and a downstream thermocatalytic reactor. The downstream thermocatalytic reactor synthesizes acrylonitrile, which is a critical precursor to structural carbon fiber, from the C_2H_2 + HCN mixture that elutes from the plasma. Remarkably, the plasma synthesis of C_2H_2 + HCN from CH_4 + N_2 is highly selective. We have been able to achieve >95% methane conversion with >90% nominal yield of a stoichiometric mixture of C_2H_2 + HCN. Downstream of the plasma in the thermocatalytic reactor, selectivity is somewhat challenging, but yields of the desired acrylonitrile in the range from 20 to 40% based on C_2H_2 + HCN have been achieved at the time of writing. For technoeconomic context, the results will be compared against the industrial standard SOHIO ammoxidation process for the synthesis of acrylonitrile. Furthermore, I will take this opportunity to reflect on the prospect of running a gas-phase synthesis process at a reduced pressure of approximately 0.1 bar and a production rate of minimum 10,000 tons per year.

3:00pm **PS1+AS-WeA-3 Kinetics of Hydrocarbon Decomposition in Plasmas Operating Up to 5 bar***, **Norleakvisoth Lim,** M. Gordon,* University of California at Santa Barbara

Hydrogen is a promising energy carrier to replace fossil fuels in response to the rise in global warming from CO_2 greenhouse gas emissions. Unfortunately, hydrogen is predominantly produced industrially via steam methane reforming, where the reaction itself and process heating requirements generate CO_2. Direct methane pyrolysis for hydrogen generation has recently regained interest due to its potential for net zero CO_2 emission. This process requires high operating temperatures due to high C–H bond energies (4.55 eV for methane) and collateral issues such as catalyst poisoning via coking. As an alternative, plasma–based conversion of methane to hydrogen and carbon (as well as other hydrocarbons) is an attractive process due to its potential ability to generate reactive species that can overcome activation barriers, improve CH_4 conversion, and use less energy than required for water electrolysis. Thus, understanding the mechanism and kinetics of CH_4 dissociation in thermal and non-thermal plasmas is a crucial step to evaluate the efficacy of plasma conversion of hydrocarbons.

This talk will highlight conversion, selectivity, and kinetics measurements of plasma-based decomposition of CH_4 and C_2 hydrocarbons using various plasma excitation schemes (AC arc and nanopulse) at pressures up to 5 bar in a batch configuration with different electrode gaps. H_2 selectivities up to 80% were observed in AC-excited thermal arcs, with specific energy requirements (SER) decreasing with increasing pressure to ~300 kJ/mol CH_4. In general, plasma-based conversion has fast rates and seems to not encounter the typical pseudo-equilibrium limit, i.e., due to hydrocracking of products back to CH_4, that is typically encountered with thermal pyrolysis of CH_4 at temperatures from 900-1300 °C. Other CH_4 decomposition products (<30 mol %) observed include C_2H_2 and C_2H_4, and plasma-decomposition of C_2H_4 was also studied. Product distribution with pressure and various CH_4:H_2 ratios will be discussed, along with characterization and management of the solid C product. This work suggests that higher operating pressures can potentially improve the efficiency of plasma conversion of hydrocarbons.

3:20pm **PS1+AS-WeA-4 Plasma Pyrolysis of Liquid Hydrocarbons to Produce H_2 and Solid Carbon***, N. Lim,* ***Michael Gordon,*** University of California at Santa Barbara

Understanding and engineering reacting systems that enable more sustainable use of our natural resources is central to both reducing the risks associated with CO_2 emissions and making the long-term transition to a more circular, sustainable, and electrified economy. Moreover, developing technologies to leverage the energy density of liquids to produce clean H_2 and solid carbon without CO_2, could be game changing. In this work, we investigate the potential of directly exciting plasmas in liquid hydrocarbons to create unique, multi-phase reaction environments, i.e., environments where plasma (ionized gas), gaseous H_2, gaseous and liquid hydrocarbons, and solid carbon are all present simultaneously, to produce clean H_2 and carbon. The ultimate target is direct transformation of liquid hydrocarbons to gaseous H_2 and solid, easy-to-separate carbon using electricity that can be provided from any source and/or points of use.

As a proof of concept, we have recently demonstrated that it is indeed possible to strike and sustain plasma discharges in liquid hydrocarbons such as hexane, to simultaneously generate gaseous H_2 and solid carbon at high rates. Significant H_2 generation along with small amounts of other light hydrocarbons was observed. Initial, un-optimized experiments have been promising: a single pin-to-pin AC-driven, high voltage plasma discharge running at ~18 W (estimated from the plasma current-voltage transient) in liquid hexane produced ~80-100 sccm of H_2, which is equivalent to an energetic input of ~ 240 kJ/mol H_2 = 33 kW*hr/kg H_2. This energy requirement for an un-optimized system is considerably lower than for water electrolysis (40 kW*hr/kg H_2 (theoretical), but 60 kW*hr/kg H_2 in practice), and promisingly competitive with other plasma-based hydrocarbon conversion processes. Preliminary experiments show that (i) the plasma is not simply vaporizing the liquid - so the system's specific energy input (SEI) is preferentially driving hydrocarbon cracking; (ii) small amounts of C_2-C_4 products are also produced, where selectivity depends on plasma operating conditions; and (iii) the liquid hydrocarbon phase immediately turns yellow and then quickly black due to rapid formation of suspended carbon particulates. Hydrocarbon conversion, reaction rates, and characterization of the gas (MS), liquid (GC/MS), and solid (C/H analysis, SEM, Raman) phase products as a function of plasma operating conditions and hydrocarbon source will be discussed.

4:20pm **PS1+AS-WeA-7 Plasma-Surface Interaction in CO_2 Containing Plasmas***, **Olivier Guaitella,** E. Baratte,* Ecole Polytechnique - CNRS, France*; V. Guerra,* Instituto Superior Técnico, Portugal*; D. Sadi, S. Bravo, C. Garcia-Soto,* Ecole Polytechnique - CNRS, France*; T. Silva,* Instituto Superior Técnico, Portugal **INVITED**

The use of Non Thermal Plasmas to convert CO_2 is a very promising way of meeting environmental challenges. However, there are two main obstacles to their use and optimisation:

i) the complexity of the kinetics of these plasmas makes it very difficult to predict their chemical reactivity,

ii) while it is relatively easy to dissociate the CO_2 molecule in a plasma, it is difficult to avoid reverse reaction mechanisms that reduce the energy efficiency of conversion.

To address the first point, complementary experimental set-ups have been developed in this work to enable step-by-step validation of 0D kinetic models including electronic, vibrational and chemical kinetics. This systematic approach relies on discharges as simple as pulsed glow discharge and radiofrequency discharges in batch reactor, monitored with in situ time resolved absorption spectroscopy. Thanks to these studies, models of pure CO_2 but also, CO_2/N_2, CO_2/H_2 and CO_2/CH_4 have been thoroughly validated against a large range of experimental conditions. Once these plasma sources have been well characterized, they can be used to study the fundamental mechanisms of plasma-catalyst interaction. The combination of a cold plasma and a catalyst is indeed the solution most often proposed to overcome reverse reaction processes and improve selectivity and energy efficiency. However, the design of materials truly capable of benefiting from the vibrationally or electronically excited species of the plasma relies on an understanding of these mechanisms.

In addition to plasma-catalysis, new concepts are currently emerging for continuously shifting chemical equilibria in the plasma phase, thereby improving yields.The use of ionic membranes (perovskite or Yttrium Stabilized Zirconia) or water used as solvent opens up new routes for improving plasma CO_2 conversion processes, but once again raises the question of how these plasmas interact with complex surfaces. Examples of these approaches will be given.

5:00pm **PS1+AS-WeA-9 Study of Plasma-Catalyst Surface Interactions for Methane Dry Reforming**, ***Michael Hinshelwood***, *G. Oehrlein,* University of Maryland, College Park

Plasma enhanced dry reforming of methane (DRM) at atmospheric pressure is a promising technique for converting greenhouse gases (CH_4 and CO_2) into syngas (H_2 and CO), which can be further used for producing fuels and chemicals. The exact mechanism of enhancement of DRM due to plasma is not fully understood, however plasma-generated reactive species are thought to play an important role. Enhancement in DRM can take the form of increased product formation or reduced carbon coking which can deactivate the catalyst. We use a remote plasma-catalysis setup that enables the study of certain plasma-catalyst interactions by infrared spectroscopic methods [1]. Species adsorbed on the catalyst surface are analyzed in-situ using Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), while gas phase products from the interaction are analyzed with Fourier Transform Infrared Spectroscopy (FTIR). The catalyst used is Ni, commonly used for dry reforming reactions, on a SiO_2/Al_2O_3 support. The catalyst is exposed to either Ar/CO_2 or Ar/CH_4 plasma, while other gas mixtures are introduced into the reaction chamber downstream from the plasma. This allows for evaluation of the effect of reaction species specific to either gas. DRIFTS measurements reveal that exposure to CH_4 plasma results in the buildup of CH_2 (2930 cm^{-1}) and CH_3 (2960 cm^{-1}, 2860 cm^{-1}) containing species on the catalyst surface. Build-up of such species also occurs during catalyst coking and deactivation. Exposure to CH_4/Ar plasma may be able to replicate coking at low temperatures where reaction rates are lower and surface mechanisms easier to resolve. If CH_n (n=1-3) buildup at room temperature is followed by Ar plasma exposure, the CH_2 and CH_3 surface coverages are reduced at similar and temporally decreasing rates, but not eliminated. Comparing the effect of Ar plasma and Ar/CO_2 plasma on surface CH_n, is used to evaluate the potential of Ar/CO_2 plasma to reduce catalytic deactivation during dry reforming. Our setup allows for variation of the catalyst temperature to test the impact of plasma on DRM at various degrees of catalyst activity. Increased understanding of the time-dependent relationship between downstream products (FTIR) and surface adsorbed species (DRIFTS) will shed light on the plasma enhancement of DRM to inform development of future systems.

This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Fusion Energy Sciences under award number DE-SC0020232.

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5:20pm **PS1+AS-WeA-10 Silver Nanoparticle Synthesis in Low-Pressure Plasmas: The Roles of Free Electrons and Photons**, ***Chi Xu***, *J. Held, H. Andaraarachchi, U. Kortshagen,* University of Minnesota

The interactions of plasmas with liquids enable considerable electron and vacuum ultraviolet (VUV) photon fluxes to the solution surface, contributing to subsequent reduction processes and emerging as a novel technique of nanomaterials synthesis. To date, the solvated electrons were mostly proposed to be the critical reducing agent while the effect of photon-driven reactions on nanoparticle synthesis has not been fully understood. In this work, we use glycerol, a major co-product of biodiesel production as the solvent. Using this solvent, we investigate the silver nanoparticle formation in silver nitrate ($AgNO_3$)-glycerol solutions delivered as droplets to a low pressure nonthermal plasma, opening new synthetic pathways over previous bulk reactions. We demonstrate that this system allows the formation of monodispersed sub-20 nm silver nanoparticles. By inserting crystal filters having various cut-on wavelengths between the plasma and the glycerol droplet, UV radiation from the plasma-liquid emission at wavelength ranges between 150 and 280 nm is differentiated, while plasma-generated electrons are prevented from reaching the droplet. To quantify the nanoparticle yield, the final silver ion concentration was measured using a colorimetric method. We find that UV radiation contributes ~ 70% of the integral plasma effect in reducing silver ions to atoms, likely driven by H radicals attributed to the photodissociation of glycerol with an energy threshold of ~ 5 eV. The UV emission was traced to originate from carbon species released into the plasma from the glycerol solvent. The effects of aldehydes are minimal, which was evaluated by scavenger study and colorimetric assay kit, respectively. Using water as the solvent instead, silver nanoparticle formation in aqueous solutions instead of glycerol does not exhibit a strong dependence on UV emission under the same operating conditions.

The research was sponsored by the Army Research Office and was accomplished under Grant No. W911NF-20-1-0105.

5:40pm **PS1+AS-WeA-11 Plasma Synthesis of Hydrogen from Ethanol Solution**, *D. Lojen,* Université libre de Bruxelles, Belgium*; T. Fontaine,* Université libre de Bruxelles/ University of Mons, Belgium*; L. Nyssen,* Université libre de Bruxelles/Ghent University, Belgium*; D. Petitjean,* Université libre de Bruxelles, Belgium*; R. Snyders,* University of Mons, Belgium*; N. De Geyter,* Ghent University, Belgium*;* ***Francois Reniers***, Université libre de Bruxelles, Belgium

In the quest for green energy sources, hydrogen is often presented as the fuel of the future. However, as such, hydrogen must be synthesized. Among the many synthesis routes, those which don't directly produce CO2 are privileged. In this regard, water electrolysis, plasma splitting or pyrolysis of methane are intensively explored, sometimes already at the industrial or preindustrial scale. However, all routes present advantages and drawbacks. For instance, plasma splitting of methane has to deal with the removal of solid carbon from the reactor, and water electrolysis suffer from the high intrinsic energy cost to break the water molecule into H2 and O2. In this paper, we present preliminary results of the plasma induced splitting of liquid ethanol, using a nanopulsed generator, as this route could be an intermediate between the high energy cost of water splitting, and the solid carbon problem evidenced in CH4 plasma. Moreover, ethanol could be from renewable sources origin, and according to previous studies, its main oxygenated degradation product could be CO, which is useful for the chemical industry. The plasma reactor consists of a pin-to-plate electrode geometry, with the plate electrode being submerged in ethanol. The gases produced are quantified using atmospheric mass spectrometry (Hiden), and the discharge is characterized using a high speed photron camera, and electrical measurements. The main body of the reactor is glass-based, with selected entries for OES, mass spectrometry, gas inlet and outlet. Results show that the thickness of the liquid ethanol layer over the plate electrode plays a tremendous role as it generates two plasma regimes: up to 2.5 mm, the plasma is hot, with a high current and a reasonable peak voltage, whereas above 2.5 mm, the plasma changes to a DBD-like configuration, with ethanol playing probably the role of a dielectric. This induces an increase in voltage and a drop in current. Hydrogen production is directly related to the current injected in the discharge. In the hot plasma configuration, hydrogen is produced with 55% selectivity, dropping to <50 % at higher ethanol thicknesses. A change in the byproducts selectivities is also observed (C2H4, C2H2, CH4, C2H6, CO), with the change in plasma regime. Results also show the effect of the nanopulse duration and frequency and the electrode polarity.

Acknowledgements:

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Applied Surface Science Division
Room B117-119 - Session AS+CA+EL+EM+SE+SS+TF-ThM

Quantitative Surface Analysis II

Moderators: Samantha Rosenberg, Lockheed Martin, **Thierry Conard**, IMEC, Belgium, **Benjamen Reed**, National Physical Laboratory, UK

8:00am **AS+CA+EL+EM+SE+SS+TF-ThM-1 OrbiSIMS: Signal, Noise and Transmission Are Three Sides of a Metrology Triangle***, G. Trindade, Y. Zhou, A. Eyres,* National Physical Laboratory, UK*; M. Keenan,* Independent*; **Ian Gilmore**,* National Physical Laboratory, UK

In metrology, the science of measurement, a “metrology triangle” approach is used to provide a secure foundation. For example, the Quantum Metrology Triangle links Voltage, Resistance and Current through the Josephson Effect and the Quantum Hall Effect.

The OrbiSIMS[1], introduced in 2017, has become increasingly popular for biological and material sciences studies owing to its ability to give high confidence in molecular identification (mass resolving power > 240,000 and mass accuracy < 2 ppm) simultaneously with high confidence in localisation (micrometre scale spatially and nanoscale in depth). With a growing number of instruments internationally there is an increased need for metrology for reproducible measurements. We will show how Signal, Noise and Transmission form three sides of a metrology triangle that combine to enable better measurement. In a recent comprehensive study of the noise in an Orbitrap mass spectrometer, a probabilistic model was developed.[2] A region of the intensity scale is described by Poisson statistics allowing the scaling parameter, *A*, that relates ion current to the number of ions in the trap to be determined. A true signal intensity scale is then established which allows the useful yield of atoms in an implant layer to be measured. Through comparison with time-of-flight and magnetic sector instruments the fractional ion transmission is determined.[3] We will discuss how Signal and Transmission combine to understand matrix effects in biological sample preparation and how understanding Signal and Noise are important for data analytical methods.

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3. Y. Zhou, A. Franquet, V. Spampinato, G. F. Trindade, P. van der Heide, W. Vandervorst and I S Gilmore, in preparation.

8:20am **AS+CA+EL+EM+SE+SS+TF-ThM-2 Contribution of Imaging X-Ray Photoelectron Spectroscopy to Characterize Chrome Free Passivation Nano-Layer Deposited on Food-Packaging Tinplate: Composition and Chemical Environment***, E. Ros, **Vincent Fernandez**,* CNRS, France*; N. Fairley,* CASAXPS, UK*; B. Humbert, M. Caldes,* CNRS, France

To protect metal from corrosion, passivation layer are widely used in food-packaging industry. Those Nano-metric protections create a thin oxide Nano-layer on the metal surface, making it less oxidisable. Common passivation are composed by chromium oxide[1] , using hexavalent chromium as a reagent and reducing it. However, because of the toxicity of Cr(VI), European Union is gradually forbidding.Chromium Free Passivation Alternative is based on transitions metal oxides (Sn, Ti, Zr, Mn) and polymers. These samples present some roughness in few micron range observed by Atomic Force Microscopy.XPS Imaging were perform at different binding energy to allow extracting spectrum in each pixel over the eight (Mn 2p, O 1s, Sn 3d, Ti 2p,N 1s, C 1s, P 2s and Zr 3d) XPS core level process. This study show an anti-correlation between atomic concentration of Titanium and Tin Fig(1). We observe a ratio Sn oxide Sn metal homogeneous and independent of the Ti, Sn ratio More over using the vector method [2], [3] concurrently to height XPS core , we could extract two different chemical environments spectrum. The linear Least Square combination of theses 2 spectrum allow us to model 131072 regions. To extract information form XPS data on heterogynous sample the combination of XPS imaging energy scan measurement with the vector method is a promising way. These results bring the useful information about different thin layer deposition steps. Imagerie XPS results are in agreement with Raman imagerie analysis

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8:40am **AS+CA+EL+EM+SE+SS+TF-ThM-3 Cryo-Xps for Surface Characterisation of Nanomedicines***, **David Cant**,* National Physical Laboratory,, UK*; Y. Pei,* National Physical Laboratory, UK*; A. Shchukarev, M. Ramstedt,* University of Umea, Sweden*; S. Marques, M. Segundo,* University of Porto, Portugal*; J. Parot, A. Molska, S. Borgos,* SINTEF, Norway*; C. Minelli, A. Shard,* National Physical Laboratory, UK

Nanomedicines are an area of great interest for current and future pharmaceutical development. The use of nanoparticles to act as carriers for a therapeutic load has the potential to significantly improve medical outcomes, for example by allowing a therapeutic agent to circulate within the body for longer, or by allowing targeted delivery of a drug to a specific site. Such nanomedicines often rely on specific functional coatings to achieve their desired impact; for example the majority of nanomedicines currently available on the market utilise a poly-ethylene glycol (PEG) surface coating for its ‘stealth’ properties, helping nanomedicines evade the body’s clearance mechanisms. Accurate measurement of the surfaces of such nanomaterials is therefore of great importance, yet direct, quantitative surface chemistry measurements are not commonly available, and vacuum-based analysis methods such as XPS are unlikely to provide a representative measurement of the particles in their hydrated state.

Here we present to the best of our knowledge the first use of Cryo-XPS to provide direct, quantitative measurements of the surface chemistry of nanomedicines in a hydrated state. Two nanomedicine systems were measured: a drug-carrying polymer nanoparticle; and an mRNA loaded lipid nanoparticle. Both systems possessed a supposedly PEG-terminated surface, and were measured using XPS in both aqueous cryogenic state, and dry drop-cast onto a substrate. The results of these measurements clearly demonstrate that while the PEG surface cannot readily be observed in the dry state, the cryogenic measurements exhibit spectra that are consistent with the particle being measured in a hydrated condition.

9:00am **AS+CA+EL+EM+SE+SS+TF-ThM-4 Redox XPS as a Means to Address Some XPS Reproducibility Challenges***, **Peter Cumpson**,* University of New South Wales, Australia

The challenge of better understanding of increasingly-complex specimens in surface analysis has been highlighted recently[1,2,3,4]. Especially at a time of high throughput XPS instruments and broadening of the (non-specialist) user community. An AVS survey conducted in 2018 found that 65% of those responding identified reproducibility as a significant issue [5].

There is an analogy to be made with some radically–different technologies. Machine Learning makes more sense of a moving image than a single snapshot, even if the snapshot were to come from a larger, better calibrated camera. Yet somehow we expect greater calibration precision, reference data and rigorous procedures to be the only route to reliable understanding of single spectra.

Generating a sequence of spectra from a progressively chemically-modified surface can remove many ambiguities that can otherwise cause misinterpretation. Such sequences thereby help with rapid understanding of the unmodified surface. On the theme of “Two is Better than One: Breaking Barriers with Coupled Phenomena” we present results from coupled stepwise oxidation/reduction of the surface and XPS to resolve such ambiguities for a wide range of materials and problems. Gas-phase oxidation agents are used to move through the redox states of a specimen in a controllable way, taking advantage of the logarithmic growth of oxide thickness. What is more, this oxidation is easy to implement in the entry-locks of modern XPS instruments through the use of vacuum ultraviolet light (VUV) and the *in situ* generation of ozone and gas-phase hydroxide free radicals. In the past there have been many studies of how particular materials react to ozone exposure at their surfaces, often employing XPS. Here we reverse this, and use ozone (and VUV) exposure to simplify the interpretation of spectra from a wide range of unknown materials, we think for the first time.

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9:20am **AS+CA+EL+EM+SE+SS+TF-ThM-5 Sub-Nanometer Depth Profiling of Native Metal Oxide Layers Within Single Lab-XPS Spectra***, **Martin Wortmann**, N. Frese,* Bielefeld University, Germany*; K. Viertel,* Bielefeld University of Applied Sciences and Arts, Germany*; D. Graulich, M. Westphal, T. Kuschel,* Bielefeld University, Germany

Many metals form nanometer-thin self-passivating native oxide layers upon exposure to the atmosphere, which affect their interfacial properties and corrosion behavior. Such oxide layers are commonly analyzed by X-ray photoelectron spectroscopy (XPS). Here we propose a simple and accessible depth profiling approach for oxide layers with sub-nanometer depth resolution from single lab-XPS spectra. Metals and their oxides can be distinguished by a binding energy shift to quantify their distinct signal contributions. Analogous to the widely used Hill equation we utilize the known photoelectron's inelastic mean free path to calculate the characteristic oxide layer thickness. However, in contrast to the Hill equation we analyze not only one, but all orbital energies in the XPS spectrum to develop a model that accounts for a depth-resolved concentration profile at the oxide-metal interface. The proposed model not only improves the accuracy and reproducibility of earlier methods but also paves the way for a more holistic understanding of the XPS spectrum.

9:40am **AS+CA+EL+EM+SE+SS+TF-ThM-6 A Tag-and-Count Methodology Based on Atomic Layer Deposition (ALD) and Low Energy Ion Scattering (LEIS) for Quantifying the Number of Silanols on Fused Silica***, **Josh Pinder,*** Brigham Young University

The concentration of surface silanols governs many of the properties of glass and fused silica surfaces including surface wetting, surface contamination rates, and thin film adhesion. Indeed, the concentration of surface silanols is impactful for diverse fields such as atomic layer deposition (ALD), chromatography, catalysis, and displays. Accordingly, various analytical and theoretical methods have been employed to determine the number of silanols on surfaces, including density functional theory, FTIR, thermogravimetric analysis, and temperature programed desorption mass spectrometry. However, many of these methods are better applied to particulate materials than surfaces. In this presentation, we discuss a method for directly

measuring the concentrations of surface silanols on silica-containing surfaces via a tag-and-count methodology. This approach is based on tagging surface silanols by ALD via a single pulse of dimethylzinc or diethylzinc and then quantifying the number of tags (zinc atoms) using high

sensitivity-low energy ion scattering (HS-LEIS). Our method yielded the literature value for both fully hydroxylated fused silica and also fused silica that had been heated to 500, 700, and 900 C. We see this capability as enabling for all who work with glass, fused silica, and silicon wafers,

including for ALD.

11:00am **AS+CA+EL+EM+SE+SS+TF-ThM-10 ASSD Peter M. A. Sherwood Mid-Career Professional Awardee Talk: Providing Fundamental Mechanistic Insights Into Single-Site Catalytic Reactions***, **Jean-Sabin McEwen**[1],* Washington State University **INVITED**

The single atom limit achieves the ultimate degree of material efficiency for supported metal catalysts. To this end, the ability to create highly dispersed, single-site catalysts, which are highly efficient and have low cost, is very much desirable. While single atom sites can be created, there is still disagreement over whether the single atom sites are indeed catalytically active or if the observed catalytic activity of single-site catalysts is due to metal nanoparticles either unobserved during initial microscopy studies or formed upon exposure to catalytic conditions. Such disagreements create a crucial need for the development of well-defined single-site catalysts with an accurate theoretical model in order to correctly determine the chemical nature of the catalytically active sites. To this end, we provide new atomistic insights regarding the "44" Cu surface oxide through the integration of synchrotron-based X-ray Photoelectron Spectroscopy (XPS) measurements, Synchrotron X-ray Diffraction measurements (SXRD), Scanning Tunneling Microscopy (STM) and Density Functional Theory (DFT) techniques. We also quantify the low-temperature CO oxidation kinetics on Pt single-site catalysts supported on the "29" Cu surface oxide. The "29" Cu surface oxide is a high coverage chiral structure that arises when we further oxidize the "44" structure. Using STM, CO temperature programmed desorption (TPD), and DFT techniques, we determine that an accurate model for the "29" Cu oxide surface is formed from the growth of a Cu_xO layer formed from 6 fused hexagonal rings above the Cu (111) surface where 5 oxygen adatoms are added at the center of the Cu_xO rings. Furthermore, we determine the state of the Pt single atoms before, during, and after reaction through a combination of theoretical and experimental techniques. We also correlate ambient pressure experiments, surface science measurements and first principles-based calculations to demonstrate that Pt/Cu(111) single-atom alloys (SAAs) oxidized with varying degrees of O_2 exposure can be reduced with H_2 with reasonable kinetics (hours). This is in contrast to oxidized pure Cu(111) where such reduction is very slow (days). We further contrast the catalytic properties of Rh/Cu(111) SAAs with varying degrees of O_2 exposure to the those of Pt/Cu(111) SAAs. Finally, we report the effects of a copper oxide thin film toward the segregation of noble metal single-atoms on Cu (111) using DFT.

11:40am **AS+CA+EL+EM+SE+SS+TF-ThM-12 Beyond the Physical Origin of the Shirley Background in Photoemission Spectra: Other Predictions of the Interchannel Coupling with Valence Band Losses Mechanism***, **Alberto Herrera-Gomez,*** CINVESTAV-Unidad Queretaro, Mexico

The physical mechanism proposed in our 2017 paper about the origin of the Shirley background in photoemission spectra[1] es based on interchannel coupling[2] but with the important addition of energy losses in the valence band.[3] Besides the Shirley background, it is possible to derive other predictions of the interchannel Coupling with Valence Band Losses mechanism (ICLM). Two of them are discussed in this paper: 1) the quantitative relation between Auger peaks and the Shirley background and 2) the conduction-band-like structure of the extended region of the Shirley background.

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12:00pm **AS+CA+EL+EM+SE+SS+TF-ThM-13 Aging of Hydrophilicity in a Nano-Textured SS316 Thin Film Fabricated by Magnetron Sputtering***, **Pakman Yiu,*** Ming Chi University of Technology, Taiwan*; J. Chu, J. You,* National Taiwan University of Science and Technology, Taiwan

According to the structural zone model by J.A. Thronton[1], we may manipulate the surface morphology of a thin film by altering the deposition temperature and vacuum. Therefore in this study, we prepared a series of SS316 thin film by magnetron sputtering under different Argon working pressure. Resultant thin film possessed a pressure dependent nano-textured surface which was dependent on working pressure. Furthermore, we discovered that the textured surface was highly hydrophilic (water

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[1] **ASSD Peter Sherwood Award**

contact angle <15 degrees). The hydrophilicity could be attributed to the combinitorial contribution of surface roughness and capillary effect. However, we also discovered that the hydrophilicity aged with time, where after 21 days the surface turned hydrophobic with water contact angle >90 degrees. XPS studies on both as-deposited and 21-days stored sample films revealed that there was a Carbon-rich surface layer on the surface which grew with time. Interestingly when we tried to clean the surface with Argon atmospheric plasma, the hydrophilicity was almost fully restored. Results revealed that the aging of hydrophilicity may due to the fact that nano-surface texture gathers hydrocarbons in the atmosphere, which eventually formed an extra film that altered the surface wetting property. Understanding the aging mechanism and method of ecovery may contribute to the development of a long-lasting hydrophilic surface, which is very useful in applications such as self-cleaning surface and medical apparatus[2,3]

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Plasma Science and Technology Division
Room A106 - Session PS2+AS+SS-ThM

Plasma-Surface Interactions I

Moderators: Lei Liu, Lam Research Corporation, **Pingshan Luan**, TEL Technology Center America

11:00am **PS2+AS+SS-ThM-10 Remote Plasma-Activated and Electron Beam-Induced Etching of Ruthenium and Its Comparison to Tantalum***, Yudong Li*[1]*,* University of Maryland College Park*; C. Preischl, M. Budach, H. Marbach, D. Rhinow,* Carl Zeiss SMT, Germany*; G. Oehrlein,* University of Maryland College Park

Refractory metals are of importance in microfabrication, which necessitates patterning of these materials. One issue is to reduce near-surface modifications of materials during processing, which is often due to ion bombardment and atomic mixing. Recently, we have developed a novel technique of combining electron beam (ebeam) and remote plasma (RP) for materials processing [1, 2]. Material damage is significantly reduced since energetic ion bombardment is prevented. The RP generates reactive neutral precursors and the ebeam provides energy deposition to enable further precursor-materials interactions.

Here we investigate the effects of ebeam and RP on Ru and Ta with the goal of selective etching. The simultaneous irradiation of ebeam and RP with Ar and O_2 as the feed gas induces Ru etching. The Ru ER increases with emission current, electron energy, and O_2 flow rate, while it shows less dependence on RP power. A pretreatment step by ebeam/RP or RP only with $Ar/O_2/CF_4$ significantly enhances the subsequent Ru ER induced by ebeam/RP with Ar/O_2. This effect is likely associated with the reactor wall passivation by the introduction of CF_4 through RP, which reduces recombination of O atoms on reactor surfaces. For Ta, RP with fluorine-rich $Ar/O_2/CF_4$ induces Ta etching at a high rate. If instead an O_2-rich gas mixture is used, we observe Ta oxidation. The RP sustains the spontaneous Ta etching by generating F which interacts with Ta and forms volatile tantalum fluoride. Contrary to the Ru metal, where the ebeam induces etching, the ebeam is found to promote oxidation of Ta. The opposite roles of ebeam on Ru and Ta and the sensitive dependence on CF_4 flow rate of Ta etching provides the opportunity to achieve Ru over Ta etching selectivity.

We gratefully acknowledge the financial support of this work by Carl Zeiss SMT GmbH

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11:20am **PS2+AS+SS-ThM-11 Plasma Surface Ionization Wave Interaction with Single Channel Structures***, Joshua Morsell, S. Shannon,* North Carolina State University

The interaction of atmospheric pressure plasma jets (APPJ) with materials has found promising applications in the fields of plasma medicine, catalysis, and material treatment. One area of interest is the surface ionization waves (SIW) present in these plasmas. SIWs interactions with complex interfaces is critical to these applications and require further study. A complex interface is any target with non-uniform electrical properties and/or non-planar surface morphology. The focus of this work is to study how surface ionization waves interact with single channel structures in dielectric media. The results show that the fraction of the SIW that escapes the channel is dependent on both driving voltage and channel width.

The plasma source in this study is an APPJ powered by a nanosecond DC pulse of positive polarity with helium as the working gas as used in [J. Morsell et al., J. Phys D: Appl. Phys. 56 (2023), 145201]. Voltage and current data are collected via integrated current and high voltage probes at the source head. Time resolved ICCD imaging is used to image SIW propagation. The single channel targets consist of a 25 x 50 mm glass slide which has had a single channel etched across its minor axis. There are six total channel samples with different widths and depths. These samples are mounted to a target stage, which has another glass slide with an optically transparent conductor acting as a ground plane allowing imaging through the substrate.

SIW velocities in the system have been measured. The first is the SIW velocity within the channel, the second is the radial velocity of the portion of the SIW that escapes the channel. Both velocities increase with increasing voltage but show no significant trends with channel geometry. Velocity magnitudes for radial surface waves are 40-70 km/s and in-channel velocities are determined to be 60-130 km/s. Total light emission from the discharge is used to determine the fraction of the SIW escaping the channel. There exists a strong dependence of SIW portioning with channel geometry and driving voltage. As voltage increases the SIW is less confined and the fraction of the SIW escaping the channel increases. As channel width increases less of the SIW is allowed to escape the channel. No conclusive trends are observed with respect to channel depth. Observation also reveals that the fraction of the escaping SIW relates to the sample area exposed to the discharge. A smaller area of the substrate is exposed to the SIW for low voltages and large geometry channels.

This work is supported by the U.S. Department of Energy, Office of Science, Office of Fusion Energy Sciences under Award Number DE-SC0020232.

11:40am **PS2+AS+SS-ThM-12 Plasma-wall Interactions: Implications for Advanced Chamber Materials Requirements***, John Daugherty,* Lam Research Corporation **INVITED**

In semiconductor device fabrication, plasma-assisted processes dominate both the deposition and etching of materials.Over 50 years of successive technology nodes have motivated innovations and continuous improvements in plasma reactor technology, and the semiconductor industry now employs a sophisticated portfolio of plasma reactors that use a wide variety of chemistry and operating approaches. Today, many aspects of the fabrication process must achieve process variations of ~1% and often must contribute particle contamination of less than one particle per wafer pass.Despite dramatic improvement in reactor design and in chamber materials, it remains challenging to achieve current variation requirements because plasma reactors still suffer from process drift, molecular contamination, and particulate contamination that originate from plasma-modification of the chamber materials. The first consideration in choosing a chamber material is the expected maximum ion bombardment energy.The plasma conditions within a single chamber are quite nonuniform, and the ion energy may fall into several ranges. Some parts experience <20 eV ions, and while these parts can be engineered for very long lifetime, challenges remain in meeting performance requirements.Other parts experience ion energies >100 eV (sometimes >1 keV in etch processes).These parts are almost always cost-sensitive consumables. There is an intermediate range of ~50 to 100 eV where there is considerable materials design complexity because of the desire to maintain process stability for thousands of wafers while operating very near the energy thresholds for ion-enhanced chemical modification of the wall material. Another design consideration is that the chamber materials must withstand a repeating sequence of multiple chemistries and plasma conditions followed by *in situ* plasma cleans using still different chemistry.The variety of chemically reactive molecules and free radicals include mixtures containing multiple halogens, hydrogen, oxygen, and depositing species from fluorocarbons, hydrocarbons, complex deposition precursors, and etch products. Recently we have adapted

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

sophisticated materials metrology to examine the materials modifications that occur throughout the lifecycle of real production parts. We have also performed control experiments that allow us to infer the dominant plasma processes that cause the materials modifications we observe on production parts used in various applications.The implications for what types of materials are suitable for different parts of a plasma reactor are explored in this presentation.

Surface Science Division
Room D136 - Session SS1+AS-ThM

Molecular Organization at Surfaces

Moderators: Eric Altman, Yale University, **Zdenek Jakub**, CEITEC

8:00am **SS1+AS-ThM-1 Supramolecular Self-assembly and Metal-Ligand Redox Assembly at Surfaces*, Steven Tait,*** Indiana University **INVITED**

The selection and positioning of specific functional groups will direct packing and stacking of organic building blocks, which determine the electronic and chemical properties of molecular thin films and semiconductors. Design of molecular ligands for metal-organic complexation at surfaces can address the long-standing grand challenge of high selectivity in heterogeneous catalysis. Our group is working to develop principles of on-surface molecular self-assembly[1] and of metal-organic complexation[2] to gain new insight into molecular layers and new chemical activity at metal single-site catalysts.[3] This work involves close collaboration with multiple research groups to synergistically combine talent in design, synthesis, sample preparation, characterization, analysis, theory, and computational modeling. We use a range of surface characterization tools to interrogate these systems under well-controlled environments, including scanning probe microscopy, photoelectron spectroscopy, vibrational spectroscopy, and mass spectrometry. We investigate systems under a variety of conditions: solution/solid interface, ultra-high vacuum, and flow reactor conditions at high temperature and high pressure. Here, I will report on recent results in several aspects of this work. We have demonstrated the impact of conformational entropy in impeding self-assembly, but that this can be overcome with appropriate selection of co-solutes. Metal-organic complexes at surfaces can be designed to achieve single-site metal centers in which we can observe redox isomerism, control of metal oxidation state, transmetallation, and chemical spillover to the support. We have transferred this design concept for single-site catalysts to high-surface-area powder oxide supports and shown that these can operate as effective catalysts in solution and under gas flow conditions. Ongoing work will seek to extend understanding of these systems to achieve molecular thin films and single-site catalysts of greater complexity.

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8:40am **SS1+AS-ThM-3 Self-Assembly Controlled at the Level of Individual Functional Groups*, Benjamin Heiner,*** *A. Pittsford, S. Kandel,* University of Notre Dame

Molecular self-assembly is a process that occurs when component molecules spontaneously organize into a specific arrangement due to the intermolecular interactions between them. These interactions are influenced by the functional groups present on the component molecules. By understanding the effects that different functional groups have on the self-assembly process, we can predict and control it. To do this, we study "families" of molecules that have a common backbone but differ in the functional groups they possess. We use a combination of experimental techniques, such as pulse deposition for scanning tunneling microscopy (STM), and a variety of computational methods to investigate the changes in self-assembly behavior that result from small modifications to the functional groups. In this talk/poster, I will present our work on a family of molecules with an indole backbone, including indol carboxylic acids, multiple isatin derivatives, and proline. By studying these molecules, we are able to gain a deeper understanding of the various intermolecular interactions that drive self-assembly in these systems.

9:00am **SS1+AS-ThM-4 Atomically-Defined, Air-Stable 2D Metal-Organic Frameworks on Graphene: How the Support Defines the System Properties*, Zdenek Jakub,*** *A. Kurowska, J. Planer, A. Shahsavar, P. Prochazka, J. Cechal,* CEITEC - Central European Institute of Technology, Czechia

The functionality of 2D metal-organic frameworks (MOFs), crucially depends on the local environment of the embedded metal, and such details are best ascertained on 2D MOFs supported on atomically flat surfaces. Here, we present three systems which are well-defined at the atomic-scale, decoupled from the metal support and stable both in ultrahigh vacuum and in ambient conditions: M-TCNQ (M = Ni, Fe, Mn) supported on epitaxial graphene/Ir(111). We show that these systems are monophase with $M_1(TCNQ)_1$ stoichiometry, and we demonstrate their remarkable chemical and thermal stability. Furthermore, by a combined experimental and computational approach we study the differences between 2D MOF systems supported on graphene and on Au(111), the prototypical surface for on-surface synthesis. We show that the Fe-TCNQ on graphene is non-planar with iron in quasi-tetrahedral sites, but on Au(111) it is planarized by stronger van-der-Waals interaction. Combined with the distinct energy level alignment with the supports, this results in significant differences in the 2D MOF properties on these two surfaces. Our results outline the limitations of common on-surface approaches using metal supports and show that the intrinsic 2D MOF properties can be partially retained on graphene. The modular M-TCNQ/graphene system combines the atomic-scale definition required for fundamental studies with the robustness and stability needed for applications, thus we consider it an ideal model for research in single atom catalysis or spintronics.

9:20am **SS1+AS-ThM-5 Using 2D COFs to Stabilize Single-Atom Catalysts on Model Surfaces: From Ultra-High Vacuum System to Ambient Conditions*, Yufei Bai,*** Indiana University*; D. Wisman,* NAVSEA Crane*; S. Tait,* Indiana University

Single-atom catalysts (SACs) combine the advantages of homogeneous and heterogeneous catalysts by limiting the reaction sites to isolated single metal atoms with well-defined chemical characters. Our group has developed a metal-ligand coordination method to stabilize SACs using 1,10-phenanthroline-5,6-dione (PDO) to coordinate with metal atoms such as Pt, Fe, and Cr. In order to further improve the stability of SACs and increase metal loading, we have synthesized single-layered covalent organic frameworks (SCOFs) on model surfaces under ultra-high vacuum (UHV) conditions or under ambient conditions. These two-dimensional (2D) networks with high thermal and chemical stability were used to confine single Pt atoms coordinated with ligands into SCOF pores. Under UHV conditions, the successful formation of the SCOF with regular hexagonal pores on the Au(111) surface was achieved by surface-mediated Ullmann radical coupling of 1,3,5-tris-(4-bromophenyl)benzene (TBB) and characterized by scanning tunneling microscopy (STM). Further sequential deposition of PDO ligand and Pt on the TBB-SCOF surface allowed the formation of single-site Pt catalysts by coordination interaction. STM images have proved the confinement of PDO in the SCOF pores, while X-ray photoelectron spectroscopy (XPS) has proven the oxidation state of Pt, which is an indication of the single atom character. Under ambient conditions, a 2D imine-linked SCOF was formed on the highly oriented pyrolytic graphite (HOPG) surface by a solid-vapor interface mechanism, which allows for a high quality SCOF with long-range order. STM characterization has shown that regular SCOF networks with negligible defects were formed on the HOPG surface with domain sizes greater than 1 µm × 1 µm. These systems which combine the COF and metal-ligand coordination strategy to stabilize SACs offer the possibility to achieve higher stability and greater loading in SACs.

9:40am **SS1+AS-ThM-6 Protein Adsorption on Mixed Self-Assembled Monolayers: Influence of Chain Length and Terminal Group*, Rebecca Thompson,*** St. Edward's University

Mixed self-assembled monolayers (SAMs) are often used as highly tunable substrates for biomedical and biosensing applications. It is well documented, however, that mixed SAMs can be highly disordered at the molecular level and do not pack as closely or homogeneously, particularly when the chain lengths and head groups of the SAM thiol components are significantly different. In the current study, we explore the impact of SAM structure and mixing ratio on the weak physisorption behavior of bovine serum albumin (BSA), which adsorbs more readily to hydrophobic, methyl-terminated SAMs. Our results suggest that once the mixture includes 50%

or more of the methyl terminus, mixing ratio alone is a relatively good predictor of adsorption, regardless of the relative chain lengths of the thiols used in the mixture. This trend persists at any mixing ratio for SAMs where methyl- and hydroxyl-terminated groups are the same length or where the hydroxyl-terminated thiol is longer. The only variance observed is at low mixing ratios (<50% methyl-terminated) for a mixed SAM where the methyl-terminated component has a longer chain length. Relative protein adsorption increases on these mixtures, perhaps due to the disordered exposure of the excess alkane backbone. Taken together, however, we do not find significant evidence that varying chain lengths for mixed SAMs prepared on polycrystalline substrates and analyzed in air have an outsized influence on nanoscopic adsorption behavior, despite molecular-level disorder in the SAM itself.

Surface Science Division
Room D136 - Session SS2+AS+TF-ThM

Thin Film Surface Chemistry

Moderators: Eric Altman, Yale University, **Zdenek Jakub**, CEITEC

11:00am **SS2+AS+TF-ThM-10 Ultrafast Exciton Dynamics of Phthalocyanine Films with Different Molecular Orientations***, Hui Ung Hwang, S. Kim, J. Kim,* Korea Research Instutue of Standards and Science (KRISS), Republic of Korea

Organic semiconductors (OSCs) have enormous potential in advanced optoelectronic devices, such as organic light-emitting diodes and organic solar cells. To achieve higher performance and functional versatility for these applications, a deeper understanding of the generation and relaxation mechanism of photoexcited excitons in molecular films is essential. In this study, we investigate the ultrafast dynamics of excitons in planar-shape molecules of phthalocyanines (Pc), which can adopt a lying-down or standing-up orientation depending on the substrate used, as shown in Fig. 1.[1] The distinct ionization-energy difference of more than 0.5 eV measured by photoelectron spectroscopy confirms that the Pc thin film on HOPG substrate grows in the lying-down direction and the Pc on ITO grows in the standing-up direction. Exciton energy and population from the molecules with these two different orientations are measured by time-resolved two-photon photoemission (tr-2PPE) with time resolution of 85 fs.In this measurement, we first pump a singlet exciton population in the Pc with a femtosecond pulse and probe its evolution as a function of delay time with an ultraviolet pulse. Singlet excitons have a variety of relaxation pathways, including diffusion between molecules, intersystem crossing to triplet states, and dissociation at the interface with metals. The tr-2PPE experiments show that the exciton relaxtion in Pc molecules with the standing-up geometry is dominated by exciton diffusionin the direction perpendicular to the substrate, resulting in relatively slow exciton relaxation. However, for Pc molecules in the lying-down geometry, the excitons undergo faster transfer to the metal interface due to aligned π-orbital overlap with neighboring molecules toward the substrate. These results imply that OSCs exhibit different exciton relaxtion dynamics depending on their orientation and suggest that for planar molecules like Pc, the lying-down geometry is more favorable for exciton transfer and dissociation to the metal interface.

11:20am **SS2+AS+TF-ThM-11 Understanding the Surface Chemistry of Oxide Thin Films by Isotope Labeling***, Yingge Du,* Pacific Northwest National Laboratory **INVITED**

Isotopic engineering is developing into a key approach to study the nucleation, diffusion, phase transition, and reaction of materials at an atomic level to reveal transport pathways, kinetics, and working/failure mechanisms of functional materials and devices. Understanding these phenomena leads to deeper insights into relevant physical processes, such as the transport and intercalation of ions in energy conversion and storage devices, and the role of active sites and supports during heterogeneous catalytic reactions. Likewise, isotopic engineering is being pursued as a means of modifying functionality to enable future technological applications. In this talk, I will present our work employing isotope labeling (e.g., ^{18}O and ^{2}H) during complex oxide thin films' (e.g., WO_3, $SrFeO_{2.5}$, and $La_{1-x}Sr_xFeO_3$) synthesis and post-growth processing to track the distribution and redistribution of the isotope tracers. Isotope-resolved analysis techniques with high spatial resolution, such as time-of-flight secondary ion mass spectrometry and atom probe tomography, facilitate the accurate quantification of isotopic placement and concentration in well-defined heterostructures with precisely positioned, isotope-enriched layers. These studies allow us to better understand the growth mechanisms, surface chemistry, and elemental diffusion under working and extreme conditions.

12:00pm **SS2+AS+TF-ThM-13 Interaction of Self-Assembled Monolayers with Atomic Oxygen During Area-Selective Atomic Layer Deposition***, **Silvia Armini**,* IMEC Belgium*; A. Brady Boyd,* School of Physical Sciences, Dublin City University, Ireland

Utilising self-assembled monolayers (SAMs) to achieve area-selective atomic layer deposition (AS-ALD) as an approach to bottom-up nanofabrication has recently gained significant attention from the nanoelectronics industry.

With the continued downscaling of feature sizes, top-down processing can no longer reach the challenging demands of the industry which requires conformal coating of high aspect ratio vias and a reduction in misalignment errors in multi-layered devices. In this work we attempt to imitate the effects of the ALD oxidation pulse experienced by the SAMs during the AS-ALD process by exposing two SAMs of different chain lengths and different functional groups, (3-trimethoxysilylpropyl)diethylenetriamine (DETA) and octadecyltrimethoxysilane (OTMS), to numerous controlled in-vacuo atomic oxygen exposures with subsequent characterisation by X-ray photoelectron spectroscopy (XPS). We monitor the sequential removal of the deposited monolayers with each successive atomic oxygen exposure for both SAMs. The etch rate is observed to be distinct for the different SAMs, the amino-terminated short chain DETA SAM reveals a linear etch rate while the longer chain OTMS SAM reveals an exponential etch rate. The results presented provide some insights into what characteristics are important for choosing the correct SAM for AS-ALD applications.

Light Sources Science Mini-Symposium
Room C124 - Session LS+AC+AS+LX+MI+TH-ThA

Facility Upgrades and Recent Capability Development

Moderators: David Shuh, Lawrence Berkeley National Laboratory, **James G. Tobin**, University of Wisconsin-Oshkosh, **Gertrud Zwicknagl**, Technical University Brauschweig

2:20pm **LS+AC+AS+LX+MI+TH-ThA-1 The Impact of Upgraded High-Brightness Synchrotron Lightsources on the Chemical Speciation of Nanoscale Heterogeneous Aggregates and Transformations***, Andreas Scholl,* Advanced Light Source, Lawrence Berkeley National Laboratory **INVITED**

ALS-U is an ongoing upgrade of the Advanced Light Source (ALS) at Berkeley Lab that will endow the ALS with revolutionary x-ray capabilities. The new storage ring will enable the production of highly focused beams of soft x-ray light that are at least 100 times brighter than those of the existing ALS. Applying this technology at the ALS will help us better understand and develop new materials and chemical systems needed to advance our research needs in energy science, environmental systems research, and biosciences in the 21st century. This will create a world-leading platform for next-generation soft x-ray and tender x-ray instrumentation.

Four beamlines with new and upgraded capabilities will become available after the upgrade. The FLEXON beamline (FLuctuation and EXcitation of Orders in the Nanoscale), a high-brightness coherent soft x-ray beamline, will provide x-ray photon correlation spectroscopy and diffraction imaging techniques to study electronic, chemical, and magnetic fluctuations in quantum materials with nanosecond temporal and nanometer spatial resolution. A new ALS-U developed tender x-ray beamline is designed to address challenges at the frontiers of diverse scientific areas, ranging from soft condensed matter and biomaterials to energy science and Earth and environmental sciences. It will offer state-of-the-art nanometer-resolved chemical imaging and resonant scattering nanoprobes, enabling operando and in situ studies of materials of K-edges of elements (Na through Ca) and the M and L edges of lanthanides and actinides. These two beamlines will be complemented by two upgraded beamlines for nanometer 3D chemical tomography based on ptychography of light elements and first-row transition metals and for high-resolution ARPES.

The high coherent flux of the upgraded ALS will drastically improve the speed, sensitivity, and spatial resolution of nanoprobes, enabling the speciation and forensic study of nanoscale constituents and contaminants via x-ray absorption spectroscopy and fluorescence detection. Chemical signatures can be correlated with morphology and compared with chemical standards. Operando experiments, for example, of liquid phase systems and studies under ambient conditions, will be enabled by specially designed sample holders and liquid cells using the high penetration of tender x-rays.

3:00pm **LS+AC+AS+LX+MI+TH-ThA-3 The Advanced Photon Source Upgrade: A transformative tool for understanding material structure.**, ***Jonathan Lang****, J. Lang,* Argonne National Laboratory **INVITED**

The APS is currently undergoing a major upgrade of the facility that will increase the brightness of the x-ray beams by factors of up to 500. This upgrade will provide transformational capabilities for examining the nanoscale structure and electronic configuration of materials and their evolution with external stimuli. This presentation with provide an update on the current status of the APS-U project, and discuss the new opportunities for imaging actinide and rare-earth compounds with this new source

3:40pm **LS+AC+AS+LX+MI+TH-ThA-5 Combining Focused Ion Beam Sectioning, Soft X-ray Spectromicroscopy, and Non-Negative Matrix Factorization to Reveal Acrtinide Chemical Speciation at the Nanoscale***,* ***Alexander Ditter****, D. Smiles, J. Pacold, D. Lussier,* Lawrence Berkeley National Laboratory*; Z. Dai,* Lawrence Livermore National Laboratory*; A. Altman,* Lawrence Berkeley National Laboratory*; M. Bachhav,* Idaho National Laboratory*; B. Chung,* Lawrence Livermore National Laboratory*; C. Degueldre,* Lancaster University, UK*; S. Donald,* Lawrence Livermore National Laboratory*; L. He,* Idaho National Laboratory*; M. Mara, S. Minasian, D. Shuh,* Lawrence Berkeley National Laboratory **INVITED**

Spectromicroscopy methods, combining the chemical insight of spectroscopy with microscopy imaging, can give a unique and informative view of a sample of interest. Scanning Transmission X-ray Microscope (STXM) spectromicroscopy is one such method, utilizing synchrotron radiation to probe electronic structure with a spatial resolution in the tens of nanometers. Specialized methods like ptychography can push the spatial resolution even lower into the single nanometer range.

Discussed here, STXM spectromicroscopy is applied to two actinide samples: spent nuclear fuel, which offers a unique insight into the complex environment of nuclear fuel undergoing burnup, and uranium oxide allowed to age in a humid environment, which serves as a demonstration of the power of this technique for nuclear forensics investigations. These samples are created by focused ion beam (FIB) sectioning to generate cross-sections of ideal thickness for soft x-ray measurements (100-200 nm). The FIB method of sample preparation also allows for the measurement of highly radioactive spent fuel without containment due to the extremely small amount of material present.

Data analysis is a key component to the understanding of spectromicroscopy results for varied samples like these. Non-negative matrix factorization (NMF) is employed to identify key components and recent efforts to improve NMF to work with noisy individual STXM spectra are outlined here. Reproducibility of the analysis is a concern (as with similar methods like multivariate curve regression) and methods to enhance both reproducibility and interpretability of the results are discussed.

Combining STXM spectromicroscopy, FIB sectioning, and NMF analysis has allowed for unique insights into actinide materials. Potential future developments utilizing this method for other samples and with advanced techniques like ptychography are also discussed.

Manufacturing Science and Technology Group
Room C120-122 - Session MS+AP+AS+TF-ThA

Machine Learning for Microelectronics Manufacturing Process Control

Moderator: Tina Kaarsberg, U.S. Department of Energy, Advanced Manufacturing Office

2:20pm **MS+AP+AS+TF-ThA-1 Human-Machine Collaboration for Improving Semiconductor Process Development***,* ***Keren Kanarik****,* LAM Research **INVITED**

Although chips have been designed by computers for decades, the processes used to manufacture those chips are mostly developed manually – a costly endeavor using highly trained process engineers searching for a combination of tool parameters that produces an acceptable result on the silicon wafer. To assess whether AI could be beneficial in accelerating process engineering innovation and reducing costs, humans and machine algorithms were benchmarked on a virtual high aspect ratio plasma etch process [Kanarik, et al. Nature 616, 707–711 (2023)]. This talk will review results and take a behind-the-scenes look at the study, which showed a “human first, computer last” approach could reach process engineering targets dramatically faster and at half the cost compared to today's approach. While human expertise and domain knowledge are essential for the foreseeable future, the results point us to a path to foundationally change the way processes are developed for manufacturing chips.

3:00pm **MS+AP+AS+TF-ThA-3 Machine Learning-based Atomic Layer Deposition***,* ***Kanad Basu****,* University of Texas at Dallas **INVITED**

Atomic Layer Deposition (ALD) is dependent on a host of process parameters. These independent parameters can be set to a particular value to create customized recipes for growing films. Although they are considered to significantly influence the ALD process, existing research does not provide a methodology to quantify the impact of these parameters on growth rate and final thickness of a film. Moreover, process parameter-based thickness estimation is a resource- and time-intensive approach, requiring numerous experiments. To address these challenges, we propose a machine learning (ML)-aware strategy that generates "feature importance maps" to determine the most critical process parameters. In our study, we utilize a Veeco® Fiji Gen2 ALD system to grow a CeO2 film. Specifically, our study is associated with 78 process parameters, which include chuck temperatures, chamber temperatures, line temperatures, precursor temperatures, gas flow rates, among others. Our approach utilizes a random forest classifier, which is identifies the top-10 features (parameters) that affect ALD processes. The proposed approach furnishes promising results of up to 99% thickness prediction accuracy using the deduced top-10 features. These results are subsequently validated using in-situ spectroscopic ellipsometry, thereby advocating its effectiveness in generating the feature importance maps. We posit that only these ten features can be utilized to monitor and control ALD processes. Furthermore, in this analysis, we demonstrate the robustness of our solution, which is independent of the type of ALD process considered - standard ALD process or temperature-dependent Temperature-Time-Thickness (TTT) ALD processes. Moreover, by monitoring just ten of the 78 process parameters, the proposed approach has implications of reduced data dimensionality (up to 87.2% reduction in feature space).

3:40pm **MS+AP+AS+TF-ThA-5 Rapid Optimization of Gap-Fill Recipes Using Machine Learning**, ***Sebastian Naranjo***, *L. Medina de Oliveira, M. Chopra,* Sandbox Semiconductor

Creating and optimizing deposition recipes for nanostructured devices is costly and time-consuming. A major source of defects and device performance degradation is the formation of interior voids. These voids can have a number of causes, including non-uniform deposition rates along the substrate surface due to imperfect seeding and/or mass transport and reaction kinetics factors, as well as critical dimension variations in the initial profile due to imperfections in preceding processing steps. For example, during electroplating, the substrate surface is seeded before material deposition is set to fill the gap. Non-conformal seedings can cause the deposited material to accumulate at different rates and lead to localized voids. Void defects can also occur in highly conformal processes such as atomic layer deposition or chemical vapor deposition due to critical dimension variations such as bowing or tapering in the pre-deposition profile. Current methods for optimizing process performance rely largely on trial and error. Here we present a cost-effective and systematic computational approach to optimize recipe conditions using Sandbox Studio AI, which employs a combination of feature scale modeling and machine learning to rapidly predict process outcomes for a given electroplating system using a minimal number of experiments. In this approach, we first use critical dimension information about the fill height and void defects from a set of experiments to calibrate a feature scale model. We then use the calibrated model to predict critical dimension outcomes for thousands of possible process parameter combinations. These predictions are used to maximize process window stability and provide recipe recommendations that minimize the formation of voids even in the presence of seeding or initial profile imperfections. The showcased approach demonstrates how computational modeling can be used to accelerate learning cycles, improve process quality, and reduce development costs.

Applied Surface Science Division
Room Oregon Ballroom 203-204 - Session AS-ThP
Applied Surface Science Poster Session

AS-ThP-1 Low-Energy Ion Scattering Intensities from Supported Nanoparticles: The Spherical Cap Model to Determine Number Density, Size, and Contact Angle*, **Kun Zhao**,* University of Washington*; D. Auerbach,* Max Planck Institute for Multidisciplinary Science, Germany*; C. Campbell,* University of Washington

Supported nanoparticles are of great importance to many technologies such as fuel processing, and catalyzed chemical synthesis, energy storage and generation, thin film fabrication, etc. Low energy ion scattering spectroscopy (LEIS) with noble gas ions like He$^+$ is a powerful tool for the characterization of nanoparticles dispersed across flat support surfaces due to its ability to probe the elemental composition in the topmost atomic layer of a surface, providing quantitative information regarding the size and number density of nanoparticles.Here, we present a derivation of the LEIS intensities expected from nanoparticles and the support material as a function of the average particle size, their number per unit area and their contact angle with the support when modeled as spherical caps of the nanoparticle material dispersed over the surface of a support. The model assumes that the ion intensities are determined only by the physical blocking of linear ion trajectories, and independent of the tilt angle of the local surface relative to the incident and scattered ion directions, an assumption we support by quantitative modelling of published data which tested tilt-angle effects. The model is a generalization to arbitrary contact angles of the hemispherical cap model which assumes 90˚contact angle and has been widely used to model spectroscopic signals from nanoparticle arrays in LEIS (and also in Auger and photoelectron spectroscopies). This new model quantitatively reveals how LEIS signals are sensitive not only to the diameter and number density of the nanoparticle, but also to their contact angle (or height : diameter ratio). With the use of additional data (e.g., from microscopies or adsorption microcalorimetry), the model presented here will enable more accurate determination of the average size, shape and number density of supported nanoparticles based on LEIS intensity measurements.

AS-ThP-2 Work Function Measurement by Ultraviolet Photoelectron Spectroscopy: Versailles Project on Advanced Materials and Standards Interlaboratory Comparison*, **Jeong Won Kim**, A. Kim, H. Hwang, J. Kim, S. Choi,* KRISS, Republic of Korea*; N. Koch, D. Shin,* Humboldt University Berlin, Germany*; Z. Zhao, F. Liu,* CAS, China*; M. Choi,* SK Hynix, Korea*; K. Lee, Y. Park,* Kyung Hee University, Republic of Korea

Since the introduction of the work function (WF) through Einstein's photoelectric effect, it has become an important parameter for characterizing material surfaces. The WF governs charge injection/collection efficiency and charge transfer at material interfaces, making WF control and measurement crucial in many electronic and optical devices. Ultraviolet photoelectron spectroscopy (UPS) has been the primary method for measuring WF over several decades. However, reported WF values strongly depend on surface treatment and measurement conditions, even for the same material. Thus, it is necessary to develop a well-prepared guide to report reliable WF values.

To address this issue, we devised an interlaboratory comparison for WF measurement by UPS and present the results of a study conducted conducted under the Versailles Project on Advanced Materials and Standards (VAMAS). Two samples, a gold film deposited on a flat Si wafer and highly oriented pyrolytic graphite (HOPG), were distributed to six international laboratories. Prior to the UPS measurements, the samples underwent common treatment processes, including instrumental settings for energy-scale calibration and bias optimization. The Au sample exhibited a WF of 5.40±0.12 eV after Ar+ sputtering in vacuum, while the HOPG sample showed a WF of 4.61±0.09 eV after mechanical peeling-off. The narrow deviation in data among the laboratories for both high and low WF values will provide a basis for establishing a new international standard for UPS in the surface chemical analysis community.

AS-ThP-3 Effect of Soft X-Ray Beam on Channel Properties of 2D-Field Effect Transistor During *operando* X-ray Photoelectron Spectroscopy*, **Ansoon Kim**, S. Choi,* Korea Research Instutue of Standards and Science (KRISS), Republic of Korea*; G. Oh, T. Kim,* Jeonbuk National University, Republic of Korea

"*Operando*", meaning under working conditions, analysis method has been developed to investigate the relationship between device performance and material properties. To examine chemical and electrical properties at the channel interface of thin film field-effect transistor (FET) under working condition, *operando* X-ray photoelectron spectroscopy (XPS) should be studied due to its surface-sensitive performance. Synchrotron radiation has been used for most *operando*-XPS studies [1,2] due to its good spatial resolution (~70 nm) compared to lab-based X-ray source (usually 10 µm). Nevertheless, synchrotron-based XPS has a limitation to perform *operando* analysis of soft materials because its high photon flux may cause sample damage. However, regarding 2D materials, in-depth researches about changes in chemical or electrical property induced by micro- or nano-focused X-ray have not been published despite of high demands and lots of interests for its *operando*-XPS studies.

In this presentation, we demonstrate whether there is a change in chemical and electrical properties of partially oxidized MoTe$_2$ and MoS$_2$ flakes induced by micro-focused lab-X-ray. In addition, we also verify whether the X-ray induced chemical changes can be accelerated by high gate voltage during conducting *operando* FET measurements. As a result of this study, we suggest a method to minimize the photon-induced damage for *operando*-XPS using lab-source that a lot of analytical researcher will use in the future.

[1] N. Nagamura et al, “Chemical potential shift in organic field-effect transistors identified by soft X-ray operando nano-spectroscopy,” *Appl. Phys. Lett.* **106**, 251604, 2015

[2] I. J. T. Jensen et al, “Direct Observation of Charge Transfer between NO$_x$ and monolayer MoS$_2$ by Operando Scanning Photoelectron Microscopy,” *ACS Appl. Nano Mater.* **4**, 3319-3324, 2021

AS-ThP-4 Transient Grating Time-Resolved PEEM to Study Charge-Carrier Transport*, **Chandni Babu**, D. Zigmantas,* Lund University, Sweden

Understanding the transport of charge carriers on surfaces enables us to get insights into a material's fundamental properties, which is also important from an application point of view. Time-resolved photoemission electron microscopy (TR-PEEM) has gained popularity in the study of ultrafast photocarrier dynamics in different materials. Here we present a novel approach for measuring the transport of photoexcited electrons at surfaces - transient grating time-resolved PEEM. In this approach, the sample is simultaneously excited by two pump pulses whose interference leads to a periodic spatial modulation of the excited electrons (1). These electrons are then photoemitted by the probe pulse and are imaged in the PEEM. The gradual decay of the spatial modulation due to transport processes can be observed, providing insights into diffusion and other transport phenomena over the short length and time scales. We are using this technique to study wurtzite InP platelets which is less explored than its thermodynamically stable counterpart- zinc blende InP. Understanding the transport properties of wurtzite InP will help in developing novel electronic and optoelectronic devices.

Reference

[1] Eichler, H.J., Günter, P., Pohl, D.W. (1986). Diffraction and Four-Wave Mixing Theory. In: Laser-Induced Dynamic Gratings. Springer Series in Optical Sciences, vol 50. Springer, Berlin, Heidelberg.

AS-ThP-5 Comparison of Commercially Available as-Received Lithium Metal Surfaces Using XPS and FTI*, **Harry Meyer**, R. Sahore, A. Westover,* Oak Ridge National Laboratory

Lithium metal is used extensively a variety of battery applications. Like all alkali metals, Li-metal is reactive with ambient air to the point of being flammable. Li-metal must be stored in either vacuum or an inert atmosphere. The Department of Energy (DOE) sponsors a wide range of battery materials related projects because of their continued and growing importance to our society. One of these projects, sponsored by the Vehicle Technology Office (VTO) of DOE, is titled “Control of Li Surfaces for Solid-State Batteries”. In this project, our goal is to understand the role of native and engineered surface layers on the cycling behavior of lithium metal in solid-state batteries. An initial step of the project was to examine native surface layers of various commercial lithium which are used by most researchers in the field. Li-metal obtained from four commercial sources was compared to Li-metal films prepared in our laboratory using thermal evaporation.

The as-prepared Li-metal film and the as-received Li-metal samples were stored in an inert Ar-filled glovebox prior to surface characterization using x-ray photoelectron spectroscopy (XPS) and Fourier transform infra-red spectroscopy (FTIR).FTIR analysis was done within the glovebox and so were never exposed to air. Samples for XPS were prepared in the Ar-filled glovebox by removing small sections from the as-received Li-metal materials and placing in a vacuum transfer holder (VTH). The VTH was sealed under vacuum in the load-lock of the glovebox, moved to the XPS laboratory, and unsealed by placing it in the vacuum load-lock of the XPS. The as-received surfaces were initially analyzed. Depth profiles were done to measure the composition as a function of depth. All samples showed a mix of Li-carbonate, Li-hydroxide, Li-oxide, and Li-carbide, but showed different distributions of each for each sample. This poster will compare the as-received surface compositions and compositions as a function of depth. This abstract has been authored by UT-Battelle, LLC under Contract No. DEAC05-00OR22725 with the U.S. Department of Energy.

AS-ThP-6 Silver and Aluminum by X-ray Photoelectron Spectroscopy (XPS)*, **Braxton Kulbacki**, S. Jafari, A. Dean, S. Ko, M. Linford,* Brigham Young University

Silver (Ag) and aluminum (Al) are important technological materials. They have also been extensively analyzed by x-ray photoelectron spectroscopy and other material characterization methods. Ag is used to calibrate the ThermoFisher K alpha XPS instrument. When calibrating the instrument using Ag, the 3d5/2 peak is placed at a binding energy of 368.21 eV. Calibration of the instrument should be performed every six months. In this poster, I show and discuss the Ag calibration peak (Ag3d5/2) as well as the Ag 3d3/2, Ag 3p3/2, Ag 3p1/2, Ag 3s, Ag 4p, Ag MNN and Ag survey scans. The sample for analysis was prepared by sputtering a silver surface. The C 1s, O 1s and Ar 2p scans are included in this poster to demonstrate both the low level of contamination and the presence of ion implanted Ar. As revealed in the C1s and O1s narrow scans, argon sputtering removed carbon and oxygen contamination from the silver surface. This poster will also show and discuss XPS of aluminum metal obtained by sputtering aluminum foil. The Al 2p peak will be shown, along with its peak fitting using asymmetric peaks that appropriately account for its spin-orbit splitting.

AS-ThP-7 Copper and Gold by X-ray Photoelectron Spectroscopy (XPS)*, **Annika Dean**, S. JAFARI, B. Kulbacki, S. ko, M. Linford,* Brigham Young University

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive analytical technique used to study the characteristics of different materials. We analyzed sputtered copper and gold using a ThermoFisher Scientific K-Alpha XPS instrument. Copper is often used in the calibration of XPS instruments, particularly the Cu $2p_{1/2}$ and Cu $2p_{3/2}$ peaks. The Au $4f_{7/2}$ peak is also used as a binding energy reference. While spectra for copper and gold are available using a variety of X-ray sources and instruments, the ThermoFisher Scientific K-Alpha XPS instrument is growing in use and popularity in the XPS community. As such, access to reference spectra taken with this instrument are an important resource. Elemental survey spectra are also useful for comparison when studying copper and gold-containing compounds, revealing changes in chemical and electronic states. Peak fitting of various signals is demonstrated, which suggests appropriate functional/mathematical forms for these signals.

AS-ThP-8 Xps Investigation of Monoatomic and Cluster Argon Sputtering of Zirconium Dioxide*, **Michael Burrell**,* Naval Nuclear Laboratory, Knolls Atomic Power Laboratory*; E. Gillman,* Naval Nuclear Laboratory, Bettis Atomic Power Laboratory

The surfaces of zirconium dioxide and yttria-stabilized zirconia (YSZ) have been analyzed using x-ray photoelectron spectroscopy (XPS) after ion sputtering with monoatomic Ar^+ or an argon gas cluster ion beam (GCIB). The O/Z ratio and new components in the Zr 3d lines show reduction to lower oxidation states when sputtered with monoatomic Ar^+, but significantly less damage is observed when GCIB sputtering is used. The damaged surface layer caused by Ar^+ sputtering can be removed by subsequent GCIB sputtering. However, the depth resolution observed in depth profiles of thin YSZ films was significantly better when Ar^+ sputtering is used. Differences in the Sn content in the oxidized Zr-4 specimen were also observed when comparing Ar^+ and GCIB sputtering, suggesting preferential sputtering. Interestingly, for YSZ the Y 3d lines showed no reduced species when sputtered with either source.

AS-ThP-10 Unlocking the Potential of Critical Rare Earth Minerals: Advanced Characterization and Analysis with XPS and RBS for Sustainable Resource Management*, **Sage Buchanan**,* Western University, Canada

As the only recognized critical mineral common to over 37 nations, rare-earth elements (REE's) have garnered increasing attention for their indispensable role in clean energy and sustainable modern living practices. As essential components of permanent magnets, light-emitting phosphors, catalytic converters, and various other materials, REE's underpin high-tech consumer electronics, green energy, and advanced medical and defense systems. The critical status of REE's stems from the growing demand for these applications, as well as the clear geopolitical significance threatening their supply chain. In order to maintain responsible resource management strategies and promote the sustainable use and disposal of REE's, it is crucial to have a comprehensive understanding of the properties and quality of REE-containing materials. In an effort to advance current methodologies surrounding the analysis and characterization of REE-containing materials, this work presents preliminary results from an in-depth X-ray Photoelectron Spectroscopy (XPS) and Rutherford backscattering (RBS) study on several REE-containing minerals of significance.

To establish robust characterization and analysis procedures, several standard samples of relevant REE-containing minerals such as monazite, bastnaesite, and xenotime, as well as the metals and their oxides will be examined via XPS. Comprehensive characterization and analysis procedures will be developed to serve as valuable reference data for future characterization of REE-containing materials. In parallel, RBS and photoluminescence studies will be utilized to develop known pure standards and investigate the depth distribution of REE implantations onto silicon wafers. Together, these techniques will provide a strong foundation for understanding the composition, electronic structure, and surface chemistry of these reference materials which can serve as benchmarks for future works and industrial applications. Understanding the role of REE's in these materials is critical for optimizing extraction and recycling processes, enhancing material performance, and identifying potential substitutes or alternatives if needed. This comprehensive approach will contribute to more efficient and sustainable use of REE's, alleviating geopolitical pressure while minimizing the environmental impact associated with the extraction and importation of REE's within and into North America.

AS-ThP-11 Computer-Readable Image Markers for Automated Registration in Correlative Microscopy*, **Peter Cumpson**,* University of New South Wales, Australia*; J. Sherriff,* University of Newcastle-upon-Tyne, UK

We present a newly developed methodology using computer-readable fiducial markers to allow images from multiple imaging modalities to be registered automatically. This methodology makes it possible to correlate images from many surface imaging techniques to provide an unprecedented level of surface detail on a nanometre scale that no one technique can provide alone.

This methodology provides the capability to navigate to specific areas of interest when transferring samples from machine to machine seamlessly. Then taking data acquired from scanning electron microscope (SEM), helium-ion microscopy (HIM), secondary ion mass spectrometry (SIMS), x-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and optical inspection tools and combining all the data acquired to then generate a 3D data representative model of a surface.

AS-ThP-12 Surface Restructuring and Stability of Perovskite Oxide Electrocatalysts Studied by Surface X-ray Diffraction and Grazing Incidence X-ray Absorption Spectroscopy*, **Alvin Chang**, R. Jana, K. Stoerzinger, Z. Feng,* Oregon State University

In recent years, the trend towards clean and renewable energy sources has led to an increased interest in water-based electrocatalysis (i.e., producing green hydrogen from water as fuels and chemicals) for energy conversion and storage, but a key barrier for efficient water splitting is the high overpotential of the sluggish oxygen evolution reaction (OER). To overcome this, earth-abundant perovskite oxides of chemical formula AMO_3 with compositional substitutions have shown drastically improved OER activities and are particularly attractive due to their high activity, low cost, high tunability of composition, and controllable electronic structures.For many metal oxides it was discovered that the surface can reconstruct under the oxidative conditions imposed by OER, forming (hydr)oxides prior to the onset of the reaction, and resulting in a different surface termination than that expected from the bulk. This restructuring is varied among materials and plays a critical role in determining the stability and activity of an electrocatalyst material during and after electrochemical cycling. Thus, understanding the drivers of transformation at electrocatalyst interfaces towards the development of materials design is a key research direction in many fields. In this work we examine the impact of electrochemical cycling on surface reconstruction of Lanthanum Nickel Iron Oxide ($LaNi_{1-x}Fe_xO_3$:x=0-0.375) and Lanthanum Strontium Nickel Iron Oxide ($La_{0.5}Sr_{0.5}Ni_{1-x}Fe_xO_3$: x=0-0.625) epitaxial thin films. Surface X-ray diffraction (SXRD) is employed to investigate the relationship between complex oxide bulk composition and terminal surface OER activity and stability. X-ray reflectivity (XRR) is used to probe the electron density of surface layers and crystal truncation rod (CTR) is used to study atomic reconstruction at the surface. In select compositions, in-situ XRR and CTR illuminate the reconstruction and amorphization process during cycling under OER conditions. Furthermore, grazing incidence X-ray absorption spectroscopy (GIXAS) is performed to capture the evolution of local coordination environments with increasing compositional substitutions and soft XAS is used to explore local electronic structures. Our findings uncover the role of underlying bulk descriptors in modulating OER performance through cycling-induced restructuring and unearth the fundamental driving forces behind surface transformations in perovskite oxide materials which will provide invaluable understanding to aid in the development of electrocatalytic surfaces under OER conditions for effective materials design towards high-performance electrolyzers and batteries for renewable energy storage and conversion.

AS-ThP-13 XPS and ToF-SIMS Depth Profile Comparison of Si Heterojunction Solar Cells

Tae Kyong John Kim, Case Western Reserve University; *K. Davis,* University of Central Florida; *I. Martin,* Case Western Reserve University

X-ray Photoelectron Spectroscopy (XPS) is one of the most widely used analysis techniques for probing surface composition as well as the composition variation with depth (e.g. depth profile). Even though XPS offers quantitative analysis, limitations do exist when using the technique for depth profiling measurement of Si Heterojunction (SHJ) Solar Cells: probe depth (7-10 nm), detection limit (0.1 atomic %), peak overlaps, inability to measure Hydrogen. Such limitations can be overcome by utilizing another surface analysis technique: Time of Flight – Secondary Ion Mass Spectrometry (ToF-SIMS). ToF-SIMS offers a shallower probe depth (< 2 nm), more compatible with carrying out fine depth profile measurements (e.g. sputter segment of 2-3 nm); the technique also offers a higher detection limit (ppm-ppb), no peak overlap issue, and ability to measure Hydrogen. This work investigates the benefits and limitations of the two techniques when probing for differences in three SHJ Solar cells: Control, Good, Degraded. Even though XPS was able to monitor changes in Indium, Oxygen, and Silicon amounts, only ToF-SIMS was able to reveal the finer differences in the profiles of all of the elements considered (Sn, In, O, B, P, N, H): 1) Indium segregation at the ITO and a-Si:H interface, 2) difference in Boron distribution, 3) difference in the relative amounts of H, B, P, N.

AS-ThP-14 Surface Analysis of Ru and Ir Thin Films after Device Fabrication Processing Techniques

Randall Wheeler, *S. Antar, A. Valenti, C. Ventrice,* SUNY Polytechnic Institute; *M. Strohmayer, J. Brewer, C. Nassar, C. Keimel,* Menlo Microsystems, Inc.

Microelectromechanical systems (MEMS) are micron scale devices with moving parts. In particular, MEMS devices can be used for radio frequency (RF) switches. Ruthenium is often used as the electrical contact material of these MEMS-based RF switches because of its resistance to oxidation at elevated temperatures. In addition, the most stable stoichiometry of ruthenium oxide is RuO_2, which is an electrically conductive oxide. As the power density of MEMS devices is increased, the rate of metal oxide formation on the surface of the metallic Ru contacts is expected to increase, which may adversely affect the performance of the device. Since iridium resists oxidation at high temperatures and also has an electrically conductive native oxide, it may be an alternative to Ru for higher temperature applications. Measurements have been made to determine the stoichiometry and thickness of the surface oxide on Ru and Ir films after typical semiconductor fabrication processing techniques such as reactive ion etch (RIE), plasma ashing processes, and annealing in air. The metal thin films are deposited on SiO_2/Si(100) substrates, and the primary analysis techniques used for this study are angle-resolved XPS and AFM.

AS-ThP-17 In-Depth Morphology/Evolution Characterization of an Obliquely Sputtered Micro/Mesoporous Si/SiO₂ Thin Film

Behnam Moeini, Department of Chemistry and Biochemistry, Brigham Young University; *D. Shollenberger, D. Bell,* Restek Corporation; *D. Fullwood,* Mechanical Engineering Department, Brigham Young University; *R. Vanfleet,* Department of Physics and Astronomy, College of Physical and Mathematical Sciences, Brigham Young Universit; *M. Linford,* Department of Chemistry and Biochemistry, Brigham Young University

In this study, we evaluate the morphology/evolution of obliquely sputtered micro/mesoporous Si/SiO_2 thin films. We utilize various microstructure characterization metrics relying on physical descriptors, and statistical functions (such as two-point correlation functions) to assess the films. Morphological analyses were performed on scanning transmission electron microscopy (STEM) images. To examine film evolution/growth, we employ contrast-enhanced STEM images. Prior to imaging, films were infiltrated with ZnO using atomic layer deposition (ALD). Our analysis of the two-point correlation function reveals a simple ellipse/spherical local pore geometry, which differs from the long-range irregular arrangement of pores. Furthermore, by analyzing the internal structure of the pores using homology metrics, we find a good correlation with the theoretical models of morphological evolution in obliquely sputtered films.

AS-ThP-18 Benefits of Cryo-XPS for Battery Analysis

Jonathan Counsell, *A. Roberts,* Kratos Analytical Limited, UK; *C. Moffitt,* Kratos Analytical Inc., UK; *C. Blomfield,* Kratos Analytical Limited, UK; *D. Surman,* Kratos Analytical Inc.

Lithium-sulfur batteries (LSBs) are attractive because of their high theoretical energy density and low cost of raw materials. However, their commercialization has been hindered by several challenges, including the volume expansion of the sulfur electrode during cycling and the shuttle effect of polysulfide intermediates. To address these issues, it is crucial to have a deep understanding of the underlying mechanisms and the chemistry of the Li-S system.In the case of LSBs, XPS can be used to determine the oxidation states of sulfur and carbon in the anode material. Sulfur can exist in a range of oxidation states, from -2 to +6. The most commonly observed oxidation states of sulfur in LSBs are +2 and 0, corresponding to elemental sulfur and lithium sulfide, respectively. The presence of higher oxidation states, such as +4 and +6, can indicate the formation of polysulfide intermediates and the shuttle effect.The oxidation state of carbon can also be probed with XPS. Carbon can exist in various chemical environments, such as sp2 hybridized carbon in graphene-like structures or sp^3 hybridized carbon in amorphous carbon. The presence of sp2 hybridized carbon can indicate the formation of conductive carbon networks, which can improve electron transport and enhance the performance of the LSB.

However, it is important to note that XPS can also introduce spectral artefacts and alter the surface chemistry of the sample. XPS can cause damage to the sample surface, leading to the formation of new chemical species that may not represent the true surface chemistry. To mitigate these effects, cryo-XPS can be used, which involves cooling the sample to cryogenic temperatures during analysis. This can stabilize the surface and reduce the formation of artefacts, providing a more accurate representation of the true surface chemistry.

AS-ThP-19 Analysis of Buried Interfaces for Device Technology by Soft and Hard X-ray Photoelectron Spectroscopy

Jennifer Mann, *K. Artyushkova, S. Zaccarine, N. Biderman,* Physical Electronics

Due to its accuracy and reliability in determining nm-thick overlayers on Si, X-ray photoelectron spectroscopy (XPS) has been utilized as a metrology technique for many years. Performing surface-sensitive XPS is more challenging with a soft X-ray source because the interfaces of interest are frequently hidden beneath metal electrodes or oxide layers.Higher energy X-ray beams have made it possible to detect photoelectron signals from deeper in the material, however most of this analysis was performed at sites with synchrotron radiation.The recent development of lab-based hard X-ray photoelectron spectrometers (HAXPES) has created new, accessible opportunities for routine analysis of technologically significant devices.

This poster will showcase the current state of the art and potential future directions for integrating HAXPES and XPS in the study of semiconductors and nanoelectronics. It will highlight the advantages of using hard X-ray sources with a lab-based high throughput fully automated spectrometer. These benefits include the ability to analyze buried interfaces, such as electronic layers located below a surface capping layer, and compositional studies in the bulk of materials and interfaces beyond the sampling depth of soft X-rays. Deeper sampling also reduces the impact of surface contamination on the photoelectron signal and enables exploration beyond the potential depth of ion sputtering-induced damage. Additionally, eliminating the overlap between Auger and major photoemission peaks is crucial, particularly for transistor devices based on GaN technology, where quantification using XPS is impossible due to the overlap between Ga Auger peaks and N 1s photoelectron peaks.

Thin films of various types are critical components of modern microelectronic products. Conducting films form the interconnect layers in all chips, and dielectric films provide electrical insulation. Angle-resolved or angle-dependent XPS and HAXPES (ADXPS/ADHAXPES) is a powerful, non-destructive method that provides a quantitative chemical composition depth profile for thin film structures with thicknesses within the XPS sampling depth - under 5-10 nm for an Al K alpha soft X-ray source and ~15-30 nm for a Cr K alpha hard X-ray source. StrataPHI can be used for metrological applications in devices to estimate the structure of thin-film stacks from this angle-dependent data.

AS-ThP-20 X-ray Photoelectron Spectroscopy Analysis of PEMWE Catalyst Layers with Focus on Catalyst-Ionomer Interface*, Jayson Foster,* Colorado School of Mines, USA*; X. Lyu,* Oak Ridge National Laboratory, USA*; E. Padgett, S. Mauger,* National Renewable Energy Laboratory*; A. Serov,* Oak Ridge National Laboratory, USA*; S. Pylypenko,* Colorado School of Mines, USA

Polymer exchange membrane water electrolyzers (PEMWEs) are an increasingly attractive clean energy technology for producing H2 for transportation fuel. Low-temperature electrolysis systems need to make significant improvements in affordability, durability, and efficiency as well as in manufacturing scalability to meet the goal of decreasing the cost of clean hydrogen to $1/kg by 2030. Development of the next generation of PEMWEs depends on further improvements of the catalyst to achieve better activity and stability, and optimization of catalyst layer structure. This study focuses on investigating PEMWE catalyst layers with focus on catalyst-ionomer interface using x-ray photoelectron spectroscopy (XPS) as it is highly surface sensitive in identifying subtle chemical differences. XPS is a powerful technique for investigation of catalyst layers. We have previously demonstrated its ability to detect small variations in fuel cell catalyst layer composition as a function of various parameters, including catalyst ink composition and electrode fabrication. However, the ionomer is typically susceptible to X-ray induced damage during data acquisition, thus analysis was conducted with a recently developed procedure in an effort to mitigate instrumental artefacts. In this talk, we use XPS to determine spatial homogeneity of the catalyst layers to evaluate the quality of the coating methods and to compare composition of catalyst layers prepared by different fabrication methods. Next, XPS is used to probe small variations in catalyst layer composition as a function of ink shelf life. And finally, differences in the catalyst layer composition are evaluated as a function of durability testing conditions. Across these studies, elemental ratios of F to Ir were used to quantitatively track surface ionomer content relative to the amount of IrO2 nanoparticles. Additionally, peak fitting of the O 1s spectrum was analyzed to provide further perspective on the catalyst-ionomer interface composition. This talk emphasizes the capabilities of XPS to advance our understanding of the catalyst-ionomer interface as related to catalyst ink properties, catalyst layer manufacturing, and catalyst layer durability.

AS-ThP-21 Correlative ToF SIMS and STEM-EDS Analysis of Platinum Coatings on Electrolyzer Porous Transport Layers*, Genevieve Stelmacovich,* *L. van Eijk, M. Coats,* Colorado School of Mines*; S. Ware, J. Young,* National Renewable Energy Laboratory*; M. Walker,* Colorado School of Mines*; G. Bender,* National Renewable Energy Laboratory*; S. Pylypenko,* Colorado School of Mines

As the United States energy infrastructure moves towards integration of a hydrogen economy, advancing electrolyzer and fuel cell technologies has become increasingly important. In Proton Exchange Membrane Water Electrolyzers (PEMWE's), the anode catalyst layer (CL), the porous transport layer (PTL), and the interface between these two layers require further optimizations. To improve this interface and mitigate degradation involving oxide formation, titanium based PTLs are typically coated with a thin protective coating, usually platinum. It is essential to characterize PTL coatings and the CL/PTL interface to ensure limited platinum use while mitigating degradation effects.

We have recently demonstrated the capabilities of ToF SIMS as a characterization technique for PTLs, specifically its ability to differentiate coatings with different thicknesses and identify titanium and platinum oxide species at the CL/PTL interface through depth profile analysis. However, quantification of coating and oxide thickness is hindered due to the morphological nature of these materials as well as lack of standards. Our recent work focuses on correlations between Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and Scanning Transmission Electron MicroscopyEnergy-dispersive X-ray Spectroscopy (STEM-EDS) results for a series of Pt-coated samples with varied thicknesses of platinum. The same amount of time was used to coat flat titanium substrates and felt PTLs, providing samples with a range of coating thicknesses. Samples were cross-sectioned with Focused Ion Beam Scanning Electron Microscopy (FIB-SEM) for STEM-EDS analysis to determine thickness of Pt coatings and assess layer morphology. ToF-SIMS measurements were conducted on the same samples to obtain depth profiles, comparing measurements from three locations on each sample to understand the reproducibility of ToF-SIMS measurements and correlate them with TEM-EDS data. This talk will discuss reproducibility, sputter rates, and depth profile time conversions along with future directions of ToF SIMS on PTLs for investigation of degraded samples.

AS-ThP-22 Using X-Ray Photoelectron Spectroscopy (XPS) to Characterize Organo-Mineral Complexes in Environmental and Synthesized Samples*, Qian Zhao,* *M. Engelhard, A. Bhattacharjee,* Pacific Northwest National Laboratory*; E. Rooney,* University of Tennessee, Knoxville*; E. Herndon,* oak Ridge Natinal Laboratory*; K. Bidas,* University of Tennessee, Oak Ridge National Laboratory

X-ray photoelectron spectroscopy (XPS) analysis is a powerful surface characterization approach to understanding the most dynamic interface of a material. The understanding of the interface of organics and minerals in soil is critical to global carbon (C) cycling as minerals play an important role in persisting soil organic matter (SOM). Yet mechanisms of the accumulation of organic matter (OM) by associating with minerals in soil are still unclear. Chemical characterization of OM that associate with minerals provides a mechanistic understanding of mineral-OM interactions. Surface characterization, such as XPS, allows us to probe the chemical states and speciation of OM on the surface of mineral particles. This work used both synthetic mineral-OM complexes and natural soil samples to investigate the chemistry of organics that associate with minerals. In the synthetic system, we employed synthetic soil habitat (SSH) platform that can simulate soil pore distribution and mineralogy, to probe OM-mineral interactions under changing biogeochemical conditions. Surface of SSH pores was pre-coated with ferrihydrite. Water extracted OM from soil flow through the SSH platform. Surface of SSH was measured before and after OM sorption by using XPS. XPS analysis found the relatively higher concentration of C in ferrihydrite-coated surface than control. Further, the deconvolution of C 1s spectra reveals that certain carbon functional groups of SOM are preferentially adsorbed to ferrihydrite-coated surfaces. In the soil system, mesh bags (5 µm) containing ferrihydrite-coated quartz, hydrous Mn oxide-coated quartz, or quartz were buried in Toolik surface soils and incubated for 7, 14, and 28 days. The incubated mineral bags were analyzed via XPS to evaluate the quantity and composition of OM compounds that associate with specific minerals as well as spatially resolved changes in Fe and Mn speciation. We found higher organic contents in ferrihydrite-coated sand than Mn and quartz. The XPS data generated by the SSH experiments and Toolik buried mineral bag analyses are combined to provide a cross-scale understanding of organo-mineral interactions that develop in thawing permafrost soils under both redox conditions and increasing frequency of freeze-thaw cycles.

AS-ThP-23 Do Different XPS Systems Give the Same Result?*, Lyndi Strange,* *D. Baer, M. Engelhard, V. Shutthanandan,* Pacific Northwest National Laboratory*; A. Shard,* National Physical Laboratory, U.K.

Analyses of the literature indicate that there is growing use of XPS in multiple fields of research, and also a growing amount of faulty data analysis appearing in the literature. With the increasing number of XPS users, it is important that significant detail is paid toward data acquisition and analysis to ensure reproducible results. In our laboratory we have instruments from three vendors. Sometimes it is necessary to collect data from the instrument that is available at the time the analysis is needed. In addition, users often take the data away and analyze it using a variety of software packages. It is useful to know if data collected on "identical" samples produces the same results when collected on different systems and using "native" and other software packages for analysis. This paper describes a simple test of data collection on three different systems and analysis using the "native" software for each system and analysis when naively exported to CasaXPS.Our simple test sample was cleaned copper foil for onwhich we collected survey spectra and high-energy resolution Cu 3p and Cu 2p data using Kratos Axis DLD Ultra, Thermo-Fischer NEXSA, and Phi Quantera spectrometers. The following analyses and data comparison were conducted for both survey and narrow window data: i) comparison of

Cu 3p and Cu 2p peak ratios, ii) Cu 3p and Cu 2p atom ratios using native software and iii) when exported to CasaXPS. In addition, we compared the full survey spectra shapes to the ideal Cu spectra provided by the National Physical Laboratory. We note that many software packages apply transmission function correction information to peak areas during analysis, not to collected data (although the NEXSA has an option of doing it either way). Good news is that using recently calibrated instruments and vendor supplied sensitivity factors, when the analysis is done consistently – using iterated Shirley background between 58.0 and 91.0 for the Cu 3p and 920.0 eV to 970.0 eV for the Cu 2p - the same quantity of Cu is indicated to better than 3% With attention to information transfer including transmission function information, and use of appropriate consistent sensitivity factors, similar results when using CasaXPS analysis.Thus, excellent consistency can be obtained in comparing data from different systems. However, consistent reporting of the steps needed for consistent data analyses are often not reported in publications thus the quality and consistency of the analyzed data is often unknown or incorrect.

AS-ThP-25 Correlative Microscopy of SIMS, Helium Ion Microscopy and XPS*, **Jake Sheriff**, I. Fletcher,* Newcastle University, UK*; P. Cumpson,* University of New South Wales, Australia

Secondary ion mass spectrometry (SIMS) is a widely used surface analytical technique to interpret surface composition. As a primary beam is raster-scanned across a surface it is possible to recreate a total ion image from the secondary ions ejected [1]. The Ionoptika J105 is equipped with two ion beams; C60 and GCIB, the resolution of the images generated by the J105 is dictated by the spot size of these beams.

The Helium ion microscope (HIM) developed by Zeiss uses a beam of He ions to generate a secondary electron image of a surface. The use of He ions as the imaging beam allows for a spot size down to <0.5nm [2]. This has allowed the HIM to take high resolution images on a submicron scale. Unusually, at Newcastle we use a magnetic-sector analyser to allow SIMS mapping of the surface as pioneered by LIST [3], giving potentially the highest spatial resolution of any SIMS instrument.

The Axis Nova X-ray photoelectron spectrometer (XPS) is capable of parallel imaging. This is done by illuminating the sample surface with x-rays then either electrostatically of magnetically projecting the electrons into the detector [4]. Using this type of imaging one can acquire a quantifiable image of the elemental distribution from a sample's surface.

All of these techniques only tell a part of a surface's story. The HIM is able to show an accurate picture of surface morphology with nanometre resolution, while the SIMS is able to give the composition of the surface at the submicron scale and XPS can quantify the elemental distribution. By combining these techniques one can put these parts together and gain a better understanding of the surface structure, be it a bacterial colony or a piece of Martian rock.

We have developed a methodology to be able to co-localise areas of interest when transferring samples between multiple different surface techniques. Then automatically correlate all the images to form an accurate representation of a surface [5]. Correlative microscopy with SIMS, XPS, and HIM, allows an unprecedented level of surface detail to be found.

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AS-ThP-27 The Utility of Surface-Induced Dissociation in Molecular Identification*, **Gregory L. Fisher**,* Physical Electronics*; S. Iida,* ULVAC-PHI, Japan

Kilo-electron volt collision-induced dissociation (keV-CID) enables the compositional identification and structural elucidation of molecules, metabolites and degradation products with 2D/3D visualization by mass spectrometry imaging (MSI). TOF-SIMS tandem MS imaging has been brought to bear for unambiguous molecular visualization in single cell-omics [1], natural product chemistry [2], metabolomics [3,4], surface modification [5], biocompatibility, high performance polymers and composites [6], 2D materials [7], electronic devices [8], catalysis [9], forensic and failure analysis, bio-medicine and pharmaceuticals [10-12]. Here, we will introduce and explore the advantages of surface-induced dissociation (SID) to assist molecular identifications together with the CID spectra. In contrast to the CID which promotes cleavage at every molecular bond, the SID is more subtle in that the bond cleavages result predominantly in the observation of functional group chemistry. While the SID and CID are generated at the same kinetic energy, the molecular energetics are distinct which can have a pronounced effect on the calibration and, hence, the putative peaks used for precursor identification.

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AS-ThP-28 Unraveling the Temperature Induced Phase Transitions of Pbo$_x$ Using Multi-Modal Characterization Approach*, **Ajay Karakoti**, V. Shutthanandan, D. Bazak, D. Nguyen, V. Murugesan,* Pacific Northwest National Laboratory

Lead acid batteries are one of the oldest commercial batteries that have proven their reliability over the years in multiple battery applications such as starting-lighting-Ignition (SLI) batteries, uninterruptible power supply(UPS), and emergency lighting etc. Despite its extensive use, limited research work in this battery technology have culminated into several research challenges that must be resolved for the further progression of this battery technology. Oxygen vacancy mediated transition of PbO_x phases (of varying stoichiometry) during electrode fabrication and during the charge-discharge process is one such unresolved problems that have perplexed the researchers for many years. Prior investigations of the PbO_x phase evolution during thermal processing using spectroscopic and diffraction methods have shown that PbO_2-Pb_3O_4 transition passes through multiple stages though the exact stoichiometry and composition of the transition phases have never been fully understood. This study uses multimodal characterization approach to identify the structure and composition of PbO_x phases during the thermally induced phase transitions. Combined high temperature X-ray photoelectron Spectroscopy (XPS) and residual gas analysis (RGA) showed that initial surface of PbO_2 is oxygen deficient, and that Pb oxidation state changes concurrently with oxygen release during heating. It is found that the oxygen evolution and corresponding oxidation state changes occur in continuous manner instead of demonstrating a transition at fixed temperature as observed using thermogravimetry analysis. XPS and RGA analysis also reveal that the phase transition can occur at a relatively lower temperatures in high vacuum conditions revealing a potential of vacuum and beam induced damage in Pb-based materials. The talk will also highlight the challenges in the quantitative XPS analysis of lead samples. Complimentary information from different characterization techniques such as Raman and NMR spectroscopy was combined to understand the thermally induced phase transition of PbO_x that could potentially relate to the evolution of PbO_x phases observed in lead acid batteries.

AS-ThP-29 Quantitative Investigation of SiP and SiGe Layers using HAXPES and ToF-SIMS*, N. Gauthier, **Olivier Renault**, E. Martinez, J. Barnes, J. Richy, J. Kanyandekwe,* CEA-LETI, France

Nowadays, "more Moore" and "more than Moore" device architectures have strongly increased the importance of novel materials thereby necessitating the availability of adequate characterization and metrology for reliable process control. For instance, the introduction of SiGe or SiP compounds used in MultiChannel Field Effect devices or raised sources and drain leads to the need for the determination of the exact composition of the resulting films. In this work, the quantification of binary materials such as SiP and SiGe has been investigated using mainly non-destructive HAXPES and ToF-SIMS. Indeed, while the main obstacle to the use of RBS is the characterization of thin films, techniques with appropriate quantification capabilities like Atom Probe Tomography and Transmission Electron Microscopy are both time consuming and suffer from a lack of sensitivity due to their highly localized analysis volume. For quantitative characterization, the conventional X-ray Photoelectron Spectroscopy (XPS) is a powerful tool. Yet, its low analysis depth remains a major limiting factor to study buried interfaces and especially in this study, since the obtained Si-based layers are oxidized in ambient conditions (or because they should be protected by metallic layers of a few nanometers). A novel lab-based hard x-ray sources (HAXPES) was used to investigate both the chemical composition at the binary material surface and the in-depth distribution of SiO_2 within the layer thanks to the increase of the inelastic mean free path of electrons with increasing photon energy (Chromium Kα, *hv* = 5414.7 eV) [1]. To confirm the composition of the materials of interest obtained by HAXPES measurements and to calculate the adequate relative sensitive factor (RSF), the same films were characterized by ToF-SIMS. However, such as for HAXPES, Secondary Ion Mass Spectrometry (SIMS) characterization of SiP/SiGe layers often suffers from matrix effects due to the non-linear variation of ionization yields with P/Ge content. This limitation can be surpassed by analyzing reference samples, by following MCs^{2+} secondary ions or using the full spectrum protocol [2]. Finally, the P and Ge (Si) compositions of the secondary ion beam were calculated and compared with the reference composition as determined by X-ray Diffraction. The repeatability of the measurements and the influence of the layer oxidation were also studied. To conclude, the in-depth composition of the layers and the thickness of surface oxide were accurately evaluated by coupling the HAXPES results with ToF-SIMS.

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AS-ThP-30 Tof-SIMS Analyses in an H_2 Atmosphere: Improvements in Thin Films Depth Profiling and Reduction of Matrix Effect

J. Ekar, ***Janez Kovač,*** Jozef Stefan Institute, Slovenia

ToF-SIMS is a very versatile and widely applicable method for precisely characterizing the molecular structure of surfaces. Still, it also has limitations, like nonquantitative analysis caused by the matrix effect, which limits the capabilities of depth profiling of thin films. Namely, chemically similar layers are challenging to distinguish in SIMS depth profiling of thin films, and interfaces between them are difficult to identify. The reason for this is a change in the ionization yields caused by chemical composition varying from layer to layer. However, there are different ways of reducing the matrix effect. Most widely applied are laser or electron beam post ionization (SNMS), metal-assisted and matrix-enhanced SIMS, dynamic reactive ionization (DRI), and the introduction of different gases into the analysis chamber (gas flooding).

We applied the gas flooding approach to reduce the matrix effect and improve ToF-SIMS depth profiling, testing different atmospheres such as H_2, C_2H_2, CO, and O_2 in the 10-5 Pa pressure range during the analysis [1]. Gas flooding with O_2 was previously used, while our group introduced the other three gases as a novelty. We achieved the best results with the H_2 gas flooding during SIMS dual beam depth profiling. H_2 atmosphere enables more straightforward and unambiguous differentiation of thin layers of metals (Cr, Al, Ti, Fe, Ni, Ag) and their oxides, different metals, and alloys with different compositions. Furthermore, the identification of interfaces becomes easier. We also did not observe a change in the sputter rate during H_2 flooding. Surface roughening caused by the ion bombardment during depth profiling was also reduced in the H_2 atmosphere [2]. This effect is more evident after longer sputtering and depends on the chemical composition of the layer of interest. We assume that this is due to surface amorphization during the sputtering process. Our recent SIMS results also show a correlation between the SIMS signals from metals in alloys when comparing alloys with different chemical compositions analyzed in the H_2 atmosphere. The O_2 atmosphere also gives better results than UHV conditions, but improvement is less pronounced than in the case of H_2 flooding. These findings bring ToF-SIMS one step closer to becoming at least a semiquantitative method for surface chemical characterization.

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AS-ThP-34 Analysis of Defective Electrical Characteristics of Metal-Insulator-Metal(Mim) Capacitor and Improvement of Leakage Characteristics

SUNG Gyu PYO, CAU, Republic of Korea

One of the most important characteristics required for RF capacitors is the minimization of the parasitic factor. The representative parasitic factor is the series resistance and the parasitic capacitance between the Si substrate and the MIM (Metal-Insulator-Metal) capacitor that can minimize this. Most compound semiconductors are equipped with MIM capacitors, and there is a trend to adopt MIM capacitors in the CMOS process. In general, when applying a PIP (Poly SiInsulator-Poly Si) capacitor, the distance from the Si substrate is 3000 to 5000 Å, and the parasitic capacitance accounts for 10 to 20% of the total capacitance, and is responsible for poly depletion at the interface between the insulator and the poly electrode. The voltage coefficient of the capacitance is also bad. Additionally, it is difficult to secure a high quality factor due to the parasitic resistance factor of Poly Si. Therefore, to overcome these problems, MIM capacitors using metal electrodes are being introduced. MIM capacitor uses a metallization layer with low resistance and no depletion as an electrode, so it can realize a high quality factor by greatly reducing the parasitic capacitance factor with the Si substrate. In the Al-based metal structure (Ti/Al/Ti/TiN or Ti/TiN/Al/Ti/TiN), siliconnitride has better interface characteristics with the metal electrode than silicon dioxide, so it can maintain stable capacitance, has low voltage dependence, and has low leakage. Current characteristics are also relatively good. In addition, compared to silicon nitride, the thickness of silicon dioxide to secure the same level of capacitance density is relatively thin, so the proportion of changes in interface properties or property degradation at pattern edges increases, so in terms of pattern size dependence, silicondioxide In the case of the MIM top electrode etch process, dummy metal cannot be inserted during MIM patterning, so the pattern density is very low (~0.1%), and the topelectrode etch condition has good etch uniformity and a large selectivity for thin Si3N4 films. Selection of the EPD (End Point Detection) signal and appropriate etch target is different for each reticle, so target control is not easy. Because metal-rich polymer occurs due to low pattern density, it is not easy to optimize post-processing conditions. In this study, we would like to present research results on the evaluation of electrical characteristics in this MIM structure and the influence and improvement of leakage current characteristics.

AS-ThP-35 Assessment of Hafnium Oxynitride ($HfO_{1-x}N_x$) and Silicon Hafnium Oxynitride ($SiHfO_{1-x}N_x$) Components in Hf 4f XPS Spectra

M. Mayorga Garay, CINVESTAV-Queretaro, Mexico*; J. Torres Ochoa,* Universidad Politecnica de Juventino Rosas, Mexico*; O. Cortazar Martinez,* ***Dulce Maria Guzman Bucio****, A. Herrera Gomez,* CINVESTAV-Unidad Queretaro, Mexico

Nitrided hafnium oxide is employed in CMOS devices. Annealing causes species migration and the growth of interface layers. A proper characterization of the chemical composition and depth profile of this type of multilayered nanofilms is essential; ARXPS is the tool of choice.

Using ARXPS, we characterized and explored the limits on hafnia nitridation through remote plasma. Hf 4*f*, Si 2*p*, O 1*s*, C 1*s*, and N 1*s* spectra were acquired before and after nitridation with various plasma power levels (500 W-2500 W). We discriminated the peak components using advanced tools such as Active Background and Simultaneous Fitting, both encompassed in the fitting software AAnalyzer®.

The Si 2*p* spectrum before nitridation shows a signal at 102.47 eV which is attributed to $Si_{1-w}Hf_wO_2$ with high hafnium content. A byproduct of nitridation is oxidation of the substrate; a peak related to SiON appears at 102.65 eV. The Si 2*p* peak in $Si_{1-w}Hf_wO_2$ shifts to lower binding energies after plasma treatment due to dipole effects. Silicon content increases in $Si_{1-w}Hf_wO_2$ and one overlapped contribution related to $Si_{1-w}Hf_wO_{2-z}N_z$ appears. Before nitriding, the Hf 4*f* spectra show peaks related to HfO_2 (17.3 eV) and $Si_{1-w}Hf_wO_2$ (17.8 eV). After nitriding, the fitting revealed two extra signals at 16.8 and 16.38 eV which are attributed to $SiHfO_{1-x}N_x$ and $HfO_{1-x}N_x$.

AS-ThP-36 A Novel Approach for Discriminating Cu^0 and Cu^{1+} in Cu 2*P* Photoemission Spectra*, A. Torres-Ochoa,* Universidad Politecnica Juventino Rosas, Mexico*; D. Cabrera-German,* Universidad de Sonora, Mexico*; O. Cortazar-Martinez,* CINVESTAV-Unidad Queretaro, Mexico*; M. Bravo-Sanchez,* Universidad de Guadalajara, Mexico*; G. Gomez-Sosa,* ***Alberto Herrera-Gomez,*** CINVESTAV-Unidad Queretaro, Mexico

The photoemission spectra of Cu 2*p* have been extensively examined because of the numerous uses of copper in electronics and catalysis. The Cu 2*p* spectra pose a particular challenge primarily since the Cu^0 and Cu^{1+} peaks overlap and share almost identical shapes and are hard to distinguish by eye or peak-fitting analysis. Cu^{1+} and Cu^{2+} often coexist. This study reveals a subtle yet significant difference in the primary signal of the Cu $2p_{1/2}$ branch. The variation in the Lorentzian width of the Cu $2p_{1/2}$ branch enables the assessment of relative concentrations of Cu^0 and Cu^{1+}. To achieve this level of analysis, advanced fitting techniques were employed, including the Block Method, Active Background, and SVSC background. The use of these tools allowed for closely fitting all the photoemission spectra. Through precise peak-fitting analysis, it was possible to quantify the relative ratio of Cu^{1+} to Cu^0 states regardless of their significant overlap and the presence of Cu^{2+} signal.

AS-ThP-37 Morphological and Chemical State Characterization of CuO Nanoparticles and Thin Films*, M. Kazi Hanium,* Department of Physics, University of Dhaka, Bangladesh*; S. Rodriguez Bonet, M. Bosco,* ***Florencia Carolina Calaza,*** Instituto de Desarrollo Tecnológico para la Industria Química, Argentina

In recent years, transition metal oxides thin films have gained a great attention from material scientists and engineers due to their different properties which in turn provide promising applications in various fields of technology. Cu_xO has beenidentified as promising materials for solar energy conversion. In addition to their favorable band gap energies that allow for the utilization of visible light, the low cost, earth abundance, and non-toxicity of Cu are additional advantages for developing Cu-based photoelectrodes However, the poor-stability problem in the aqueous solution and low efficiency of Cu_xO thin films limit their final applications. The performance of the copper oxide thin films can be enhanced by improving the crystal quality and surface morphology of the material. Among different synthesis strategies for thin film fabrications, solution-processed methods, such as hydrothermal and electrophoretic deposition, are attractive in terms of their scalability, financial advantages and eco-friendliness. This work aims to provide a critical picture of the synthesis of Cu_xO thin films and nanoparticles by solution-processed methods. Precisely controlling the synthetic strategies will be our main focus which hopefully can contribute some useful information that helps to better understand the relation between synthetic process, final morphology, and the properties of corresponding Cu_xO thin films. In summary, results will be presented for CuO nanoparticle synthesis where the materials were calcined at different temperatures ranging from 300 to 500 C, showing mainly CuO chemical composition and structure, but a hint to the presence of Cu_2O on the surface is observed by CO IR titration experiments. In the case of thin films deposited on glass by spin coating methods from copper chloride solutions, and then annealed to 300 and 400 C, CuO micro sized needles are obtained but the presence of Cl ions is unavoidable even at the highest temperature of calcination.

Applied Surface Science Division
Room B117-119 - Session AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM

Industrial Applications

Moderators: Marko Sturm, University of Twente, Netherlands, **Alan Spool**, Western Digital Corporation, **Yundong Zhou**, National Physical Laboratory, UK

8:20am **AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-1 Correlative Analysis Using Time-of-flight Secondary Ion Mass Spectrometry for Beam Sensitive Samples***, **Jean-Paul Barnes**, C. Guyot, P. Hirchenhahn, A. De Carvalho, N. Gauthier, T. Maindron, B. Gilquin, D. Ratel, C. Gaude, O. Renault,* Univ. Grenoble Alpes, CEA, Leti, France*; A. Galtayries,* Chimie ParisTech, PSL University, CNRS, Institut de Recherche de Chimie Paris, France*; G. Fisher,* Physical Electronics USA*; C. Seydoux, P. Jouneau,* Univ. Grenoble Alpes, CEA, IRIG-MEM, France **INVITED**

Time-of-flight Secondary Ion Mass Spectrometry (TOF-SIMS) is now widely used for materials analysis in domains such as semiconductor and energy applications. These challenging applications also provide access to well-controlled, custom made samples that have allowed the limits of TOF-SIMS analysis to be identified and helped in the development of correlative analysis approaches. Recent examples include combining AFM measurements with TOF-SIMS depth profiling to correct for sputter rate differences [1] or to measure mechanical or electrical properties and performing X-ray tomography prior to FIB-TOF-SIMS analysis to allow morphological and compositional data from the same volume to be visualized [2]. Currently we are working on two aspects. Firstly improving the quantification and chemical sensitivity of the technique by combining TOF-SIMS with photoemission techniques (XPS or XPEEM), and secondly trying to improve the lateral resolution by correlation with SEM and AFM measurements. Recent examples will be shown for the analysis of beam sensitive organic samples such as OLED devices, brain tissue samples after medical device implantation [3] and symbiotic microorganisms [4]. As well as the correlative aspects between techniques, we will show how tandem mass spectrometry can help in analyzing complex organic samples. In all cases the importance of sample preparation is paramount, especially for biological samples. For example, for the correlation between TOF-SIMS and XPS on OLED samples, a wedge crater protocol has been developed to allow analysis on exactly the same area of the sample whilst minimizing beam damage to the sample. Wedge crater preparation and transfer between instruments is performed under a protected environment (vacuum or inert gas) to avoid unwanted surface modifications.

Part of this work, carried out on the Platform for Nanocharacterisation (PFNC), was supported by the “Recherches Technologiques de Base” and the “CARNOT” program of the French National Research Agency (ANR).

[1] M. A. Moreno *et al. JVST B,* vol. 36, MAY 2018.

[2] A. Priebe *et al. ULTRAMICROSCOPY,* vol. 173, pp. 10-13, FEB 2017.

[3] A. G. De Carvalho *et al. Biointerphases,* vol. 15, 2020.

[4] C. Uwizeye *et al. PNAS.* **Vol 118**, e2025252118, 2021.

9:00am **AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-3 Secondary Ion Mass Spectroscopy of Battery Surface and Interface Chemistry – Metrology and Applications***, **Yundong Zhou**, S. Marchesini, X. Yao, Y. Zhao, I. Gilmore,* National Physical Laboratory, UK

Batteries are very important to achieve carbon net zero. Understanding battery materials change, electrode surfaces, solid electrolyte interphase (SEI) evolution and novel solid-state electrolyte structures is very helpful for developing better batteries. Surface chemical analysis techniques such as X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy are often used but they have their limitations. XPS analysis cannot always resolve overlapping binding energies for some key SEI elements. The SEI often has poor Raman signal intensity. These are all hurdles for battery applications.

Secondary ion mass spectrometry has great potential to study interfacial chemistry in batteries owing to high sensitivity and high-resolution imaging in 2D and 3D.In this study, we use an OrbiSIMS instrument which is equipped with two complementary mass spectrometers (MS). A time-of-flight (ToF) MS has the capability for 2D and 3D imaging using a Bi_3^+ liquid metal ion gun with a spatial resolution of up to 200 nm but with modest mass resolving power. The Orbitrap MS offers high mass resolution and mass accuracy (> 240,000 at m/z 200 and < 2 ppm, respectively). The instrument is equipped with low energy Cs and O_2 sputter beams for high resolution depth profiling of inorganic materials. It also has a Leica docking station enabling samples to be transferred using a vacuum sample transfer chamber from an argon glove box without atmospheric exposure. To improve the quality of measurements on battery materials, we have used ion implanted materials to determine relative sensitivity factors for relevant elements. We have also conducted a systematic study to optimise the OrbiSIMS depth profiling capability. These findings along with recommendations to reduce effects of signal saturation will be discussed and examples of the application to batteries will be provided. We will provide examples of the application of ToF MS and Orbitrap MS. (1,2)

1. X. Yao et al., Energy Environ. Sci., 2023, DOI: 10.1039/D2EE04006A.
2. S. Marchesini et al., ACS Appl. Mater. Interfaces, 14(2022)52779-52793.

9:20am **AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-4 Characterizing Ion Distribution at the Solid-Electrolyte Interface in Solid-State Lithium Ion Batteries with ToF-SIMS***, **Teodora Zagorac,*** University of Illinois - Chicago*; M. Counihan, J. Lee, Y. Zhang,* Argonne National Laboratory, USA*; L. Hanley,* University of Illinois - Chicago*; S. Tepavcevic,* Argonne National Laboratory, USA

Interest in solid state lithium-ion batteries as the next generation of energy storage devices has led to intense study of the chemistry, structure, and manufacturing processes for polymer electrolytes. Lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) salt is often used to introduce Li ions into the solid-state electrolyte. Lithium bis(fluorosulfonyl)imide salt (LiFSI) and lithium nitrate ($LiNO_3$) are less expensive salts with the potential to improve performance characteristics over pure LiTFSI in certain electrolyte formulations. The differences in distribution and reactivity of these different salts are still unknown but are critical to battery performance. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) imaging and depth profiling was performed to compare the distributions of Li^+ cations and $TFSI^-$, FSI^-, and NO_3^-anions across the solid-electrolyte interface (SEI) formed between the polymer electrolyte and thin lithium metal electrode. Experiments were performed on ~600 nm salt-rich poly(ethylene oxide) electrolytes with ~10 nm overlayers of vapor-deposited Li metal. Samples were probed with 30 keV Bi_3^+ from a liquid metal ion gun while depth profiling with 10 keV Ar_{1400} gas cluster ion beam to collect both positive and negative ion mass spectra. Ion distributions from the three salts and their 3D images will be presented and discussed in terms of the relative composition of their SEI layers. Chemical differences from ToF-SIMS analysis help explain the differences in electrochemical SEI formation and half cell cycling: LiTFSI and LiFSI are similar, but $LiNO_3$ presents much different electrochemical properties.

9:40am **AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-5 A Perspective on X-ray Photoelectron Spectroscopy (XPS) Peak Fitting, and Reporting of XPS Data Acquisition and Peak Fitting Parameters in the Literature***, **Matthew Linford**, G. Major, J. Pinder,* Brigham Young University

We recently reported that a rather large fraction (ca. 40 %) of the XPS peak fitting in the literature is at best suspect. In a recent Perspective article (doi: 10.1116/6.0002437) we argue that the various stake holders of the problem can act together to improve the current situation. This Perspective begins with representative examples of poor XPS peak fitting. The purpose of showing these examples is to demonstrate to the reader that we are not quibbling or arguing over subtle interpretations of the data. Increasingly, we see errors that might be classified as egregious. We argue that science is in a state of ‘pre-crisis’ more than in a state of ‘crisis’. We suggest that if too much incorrect data analysis enters the literature it may cease to be self-correcting. We note the very large number of surface and material characterization techniques available today and how this presents a challenge for scientists. Consequently, it is likely that many manuscripts are incompletely reviewed today. Graduate students and post-docs at research institutions are often given minimal training on acquiring and analyzing XPS data. High fees for instruments can limit access to them and student training. Prisoner’s dilemmas may help explain situations in science that lead to suboptimal outcomes for the community. Authors are primarily responsible for the quality of the research in their papers, not reviewers or editors. We question the wisdom of placing the names of reviewers and editors on papers. In some cases, staff scientists are not adequately recognized for their intellectual contributions to projects. Selective reviewing may allow more reviews to be performed without overtaxing the community. Reviewing at some open access journals may be inadequate.

Collaboration needs to be encouraged to a greater extent at some institutions.

10:00am **AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-6 Unsupervised and Supervised Machine Learning Applied to ToF-SIMS of an Organic Matter-Rich Mudstone with Molecular Biomarker***, M. Pasterski,* University of Illinois Chicago*; M. Lorenz,* Oak Ridge Natinal Laboratory*; A. Ievlev,* Oak Ridge National Laboratory*; R. Wickramasinghe,* ***Luke Hanley****, F. Kenig,* University of Illinois Chicago

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) imaging has been used to detect organic compounds including molecular biosignatures (biomarkers) in geologic samples (R.C. Wickramasinghe, *et al.,* Anal. Chem., 2021, 93, 15949). The spatial distribution of these biomarkers can help determine when and how these organics were incorporated into the host rock. ToF-SIMS imaging can rapidly collect a large amount of data, but molecular and fragment ions of different species are mixed together in complex mass spectra that are difficult to interpret. Here, we apply unsupervised and supervised machine learning (ML) to help interpret the mass spectra obtained by ToF-SIMS of an organic-carbon-rich mudstone from the Middle Jurassic of England (UK). It was previously shown that the presence of sterane molecular biomarkers in this sample can be detected via ToF-SIMS (M.J. Pasterski, *et al.*, Astrobiol., in press). We use unsupervised ML on field emission scanning electron microscopy – electron dispersive spectroscopy (SEM-EDS) measurements to define compositional categories based on differences in elemental abundances. We then test the ability of four ML algorithms - k-nearest neighbors (KNN), recursive partitioning and regressive trees (RPART), eXtreme gradient boost (XGBoost), and random forest (RF) - to classify the ToF-SIMS spectra using the categories assigned via SEM-EDS, using organic and inorganic labels, as well as using presence or absence of detectable steranes. KNN provided the highest predictive accuracy and balanced accuracy. The feature importance, or the specific features of the ToF-SIMS data used by the KNN model to make classifications could not be determined, preventing post-hoc model interpretation. However, the feature importance extracted from the other three models was useful for interpreting spectra. We determined that some of the organic ions used to classify biomarker containing spectra may be fragment ions derived from kerogen.

10:40am **AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-8 Probing Thin Film Interfaces at the Nanoscale by Low Energy Ion Scattering***,* ***Marko Sturm****, A. Chandrasekaran, A. Valpreda, A. Zameshin, R. Van de Kruijs, A. Yakshin, F. Bijkerk, M. Ackermann,* University of Twente, Netherlands **INVITED**

The growth of thin films with nanometer range thickness is of great importance for application topics as nanoelectronics, oxidation protection of thin films and optical coatings for X-ray applications. The performance of these coatings often critically depends on the sharpness of the interfaces between different layers. In this talk I will outline how we use Low-energy ion scattering (LEIS) to study interface formation between layers of different transition metals (TMs) and between TMs and Si.

LEIS with noble gas ions as projectiles yields surface peaks that indicate the composition of the outermost atomic layer of a sample. This makes the technique excellently suited to study whether deposition of a thin films leads to a closed layer. However, deposition of an overlayer on top of an underlayer may result in surface segregation of underlayer atoms (driven by surface energy differences or stress), such that the surface composition is not directly representative for the in-depth concentration profile. We analyzed the evolution of surface coverage versus deposited thickness for a large set of TM/TM film combinations, deposited by magnetron sputtering in a system that allows LEIS analysis without vacuum break after deposition. By applying a model that takes into account surface segregation, the interface profiles were derived from these layer growth profiles, which we call deposition depth profile. In addition, we demonstrated that the sharpness of interfaces in TM/TM film systems can be predicted by a phenomenological model with the crystal structure and surface energy of the materials as input parameter. This model in principle predicts the sharpness of the interface in any TM/TM thin film combination! [1]

Apart from surface peaks, LEIS spectra typically also contain so-called tails, caused by projectiles that, after sub-surface scattering, are reionized when leaving the sample. It was demonstrated before that LEIS tails can be used to determine thickness of various thin film systems, when the stopping power of the projectiles is known. Here, we show that LEIS tails can also be used to determine the sharpness of interfaces of few nm Si-on-W and Si-on-Mo films, by comparing LEIS measurements with Monte Carlo simulations with the TRBS code, which takes into account multiple scattering and stopping in the target. This approach allows interface characterization from a single sample, without the need to make a deposition depth profile.

References:

[1] A. Chandrasekaran, R.W.E. van de Kruijs, J.M. Sturm, A.A. Zameshin and F. Bijkerk, ACS Applied Materials & Interfaces **11**, 46311 (2019)

11:20am **AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-10 The Effect of Instrument Settings, Sample Distance, and Tilt on TofsimsSecondary Ion Intensities***,* ***Alan Spool****, L. Finney,* Western Digital

Experiments were performed to explore the effects of various instrument settings and sample placements on secondary ion intensities to better understand what factors have the greatest effect on repeatability and replicability in TOF-SIMS. A batch of magnetic recording disks used in hard disk drive manufacture, natively flat and homogeneous, were used as test samples for the purpose. As expected, by far the largest variable altering raw intensities was the LMIG tip stability. LMIG tips can have stable emission currents while still producing variable pulsed LMIG beam currents with resultant variable secondary ion counts. This variability sometimes is seen in slow current drift, but is sometimes so rapid that measurements taken directly before each measurement are not close enough in time to properly scale the measurement results. In these cases, normalization is the only solution. Secondary ion intensities were remarkably insensitive to small variations in sample height (position relative to the extractor). Far more interesting were the changes to the secondary ion intensities that resulted from tilting the sample. These effects varied amongst the secondary ions detected such that normalization did not remove them. Secondary ion emission as a function of emission angle has long been understood to be like a cosine function and to vary somewhat from ion to ion. These different angular profiles explain the differences seen in ion detection as a function of tilt. Some of these differences proved to be asymmetrical, varying depending on whether the sample was tilted toward or away from the primary ion source, an indication that in some situations some residual momentum from the initial primary ion impact onto the surface is carried into the secondary ion emission. These results have implications for attempts to do quantitative analysis on any sample that is not completely flat.

11:40am **AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-11 Evaluation of Unaltered and Irradiated Nuclear Graphite Surfaces through Integrated Traditional XPS and HAXPES Techniques***,* ***Jonathan Counsell****, L. Soomary, K. Zahra,* Kratos Analytical Limited, UK*; B. Spencer, A. Theodosiou,* University of Manchester, UK

Graphite-moderated reactors have been operational worldwide for several decades. There exists a substantial body of research in this domain, with particular emphasis on investigating the impact of irradiation damage on the graphite matrix. In order to satisfy the design and regulatory requisites of these advanced reactors, it becomes imperative to gain a deeper comprehension of the retention and transportation mechanisms of fission products within graphite.

This study outlines a technique for the precise assessment of the surface chemistry of highly-oriented pyrolytic graphite (HOPG), serving as a representative model akin to the current graphite grades utilized in the nuclear sector. We delve into the process of surface etching aimed at eliminating surface adsorbates and contaminants. This process involves the utilization of both monatomic and cluster ions, the former inadvertently causing undesirable damage to the graphite structure. Such damage is evidenced by a significant reduction in the sp2 component of C 1s. We introduce the use of UPS analysis as a straightforward means of determining the presence of sp2 characteristics in the uppermost atomic layers.

Moreover, we examine the consequences of high-energy ion implantation (Cs+) and the ensuing damage to the HOPG surface. This examination is carried out using XPS (1486eV) and HAXPES (2984eV), thereby showcasing the capability to characterize the resulting surface damage and the associated alterations within the probed depths.

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