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.

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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

Liu, Z.; Clark, A. E. An Octanol Hinge Opens the Door to Water Transport,*Chemical Science*, **2021**, *12*, 2294 – 2303. **DOI**: 10.1039/D0SC04782A.

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.

Chemical Analysis and Imaging of Interfaces Focus Topic
Room A105 - Session CA2+AS+LS+NS+SS+VT+MoM

Environmental and Energy Interfaces

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

10:40am **CA2+AS+LS+NS+SS+VT+MoM-8 Probing hydrogen bonding in aerosols, and solutions with X-Ray and vibrational spectroscopy***, **Musahid Ahmed**,* LBNL **INVITED**

Hydrogen and non-covalent bonding drive myriad processes which have enormous ramifications in molecular growth in soft systems. For instance, subtle changes in pH can drive dramatic changes in assembly processes relevant to biology, while a few degrees of change in temperature leads to enormous changes in plastic crystals, a phase change material (PCM) -- systems of significant importance in thermal science. At Berkeley lab, we have developed an integrated suite of both synchrotron (X-Ray) and non-synchrotron-based (vibrational-THz, IR, Raman) spectroscopic techniques coupled with micro-reactors and aerosol beams to establish a molecular-level understanding of bonding & dynamics in heterogeneous systems.[1-3]

Deep eutectic solvents (DESs), an important class of solutions, are considered as alternatives to conventional organic solvents and ionic liquids in many applications because they are highly biodegradable and renewable. DESs consist of a hydrogen bond donor and an acceptor and the ability to tune these hydrogen bonds to target required properties is what makes them attractive. At specific compositions, these forms a eutectic mixture which resemble many characteristics of ionic liquids and organic solvents thanks to its complicated inter and intramolecular hydrogen bonding network. Connecting PCM's and DES's are hydrogen bond networks and the changes impacted on it by including inorganic salts, which can be extended to build hydrogen bonded organic frameworks (HOF). Beyond enormous potential for new materials for energy storage, transport, and carbon capture, the study of HOF dynamics may also answer fundamental and controversial questions on the nature of hydrogen bonding, such as the invocation of anti-electrostatic forces in their formation. In this talk, I will describe new results using Raman spectroscopy coupled to aerosol-based X-Ray spectroscopy to probe such dynamics in choline chloride/glycerol, phosphoric acid and ammonium sulfate systems. These results also benefit from electronic structure calculations particularly for X-Ray photoelectron and absorption spectroscopy in providing exquisite insight at the molecular level on structural changes on the nanoscale.

1 Lu, W. *et al. Cell Reports Phys. Sci.***3**, doi:10.1016/j.xcrp.2022.100988 (2022).

2 Weeraratna, C., Amarasinghe, C., Lu, W. C. & Ahmed, M. *JPC Lett* **12**, 5503-5511, doi:10.1021/acs.jpclett.1c01383 (2021).

3 Weeraratna, C. *et al. JPC Lett* **14**, 1279-1287, doi:10.1021/acs.jpclett.2c03748 (2023).

11:20am **CA2+AS+LS+NS+SS+VT+MoM-10 The Investigation of Degraded Historic Glass Samples Using X-ray Photoelectron Spectroscopy***, G. Verhaar,* Rijksmuseum, Netherlands*; J. Vienes, N. Tennent,* University of Texas at Dallas, United States Minor Outlying Islands (the)*; **Amy Walker,*** University of Texas at Dallas

The atmospheric deterioration of glass is a well-known phenomenon and is often referred to as glass disease, weeping or crizzling. Understanding this process and the underlying chemical mechanisms are important for a number of industries from preserving historic glass objects in museums to the long-term evaluation of nuclear waste glasses. In this talk we shall discuss the use of x-ray photoelectron spectroscopy (XPS), or electron spectroscopy for chemical analysis (ESCA), to examine two fragments of heavily degraded, historic glass objects.

The two glass fragments studied originated from French wineglasses and were made available for destructive analysis by the Corning Museum of Glass. The first fragment originated from c. 1750 and is a potassium rich glass (CMG449). The second fragment was dated c. 1600-1650 and is a sodium rich glass (CMG1050). Using SEM, the thickness of the alteration layers were 60-75 µm and ~30 µm for CMG449 and CMG1050, respectively.

Two types of XPS experiments were made. In the first, the surface composition of the glass fragments was examined. Second, a non-destructive cross-section analysis was performed by rotating the sample by 90° and data taken across the fracture surface providing a depth profile through the degradation layer. For example, for CMG449 an increase in the abundance of K, Na and was observed in the first ~100 µm in agreement with other studies. For CMG1050, the atomic concentration of Na also increased as a function of depth. Little, or no, K was observed as expected for a sodium rich glass.

Further, the CMG1050 surface composition did not vary across the sample. However, for CMG449 the surface composition did vary across the sample. Three different areas were identified. The outer rim of the glass contained more K compared to the inside of the foot. The middle portion contained less Na, K and Ca overall. This is a result of the manufacture of the glass. During production, the outer rim of the foot was folded over leading to the formation of a thicker rim than the inner foot region. These changes in glass thickness and stress likely lead to the observed changes in chemical composition.

Surprisingly, we also observed carbonates and formates present in the glass; their concentration varied with position and depth across the sample. There are two potential reasons for this observation. First, during the glass manufacturing process the glass melt was not completely calcined and so some carbonate was incorporated into the glass structure. Second these species are the result of aging of the glass and form in a similar manner to the formation of carbonate salts on glass surfaces. Studies are on-going to determine the origin.

11:40am **CA2+AS+LS+NS+SS+VT+MoM-11 Studying Oil-in-Water Emulsion Interfacial Changes Using Static and in Situ Imaging***, **Xiao-Ying Yu,*** Oak Ridge National Laboratory

Bilgewater emulsion formed from the shipboard is regarded as a major pollutant in the marine environment. Bilgewater exists in a stable oil-in-water (O/W) emulsion form. However, little is known about the O/W liquid-liquid (l-l) interfacial evolution. Although some compositional information can be acquired, traditional bulk characterization approach is not capable of capturing the chemical changes at the O/W l-l interface. Surfactants are deemed essential in droplet formation, however, their roles in bilgewater stabilization are not fully understood. We have employed both static and novel in situ scanning electron microscopy (SEM) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) to study the evolving O/W interface using a NAVY bilge model for the first time. Optical microscopy was also used to confirm droplet size distribution (DSD) measurements. Our results show that the DSD of bilgewater does not change significantly without the addition of X-100 surfactants at static or rocking conditions. The in situ SEM results show that droplets coagulate even as freshly prepared emulsions. The mean DSD becomes bigger over a short course of twenty-four hours. Furthermore, both oil components and water clusters are shown to evolve over time at the O/W droplet interface by in situ liquid SIMS imaging. Of particular interest to droplet stabilization, the contribution of surfactants to the aged bilge droplets becomes more significant as the droplet size increases. The higher mass surfactant component does not appear on the droplet surface immediately while many lower mass surfactants are solvated inside the droplet. However, such interfacial information is lost when using static SIMS, because the solvent cage is collapsed during sample drying. We have provided the first three-dimensional images of the evolving O/W interface and demonstrated that in situ surface chemical mapping is powerful to reveal the complex and dynamic l-l interface in the liquid state. Our observational insights suggest surfactants are important in mediating droplet growth and facilitating effective separation of bilgewater emulsion. To conclude, our recent findings demonstrate the importance of using in situ molecular imaging to study the evolving l-l interface and offer new insights into the physicochemical changes of emulsions.

Chemical Analysis and Imaging of Interfaces Focus Topic
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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

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 $1\text{-}6\times10^6$ 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.

[1] S.V. Verkhoturov et al. J. Chem. Phys. 150 (2019)

[2] R.D. Rickman et al. Phys. Rev. Lett. 92, 047601 (2004)

[3] D.S. Verkhoturov et al. Biointerphases 11, 02A324 (2016)

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Polish National Science Center 2019/33/B/ST4/01778, PLGrid Infrastructure Grant

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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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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Chemical Analysis and Imaging of Interfaces Focus Topic
Room Oregon Ballroom 203-204 - Session CA-TuP
Chemical Analysis and Imaging of Interfaces Poster Session

CA-TuP-1 Combined Spectro-Electrochemical Methods to Investigate Electrochemical Corrosion in Real-Time*, **Matteo Olgiati**,* CEST GmbH, Austria

Many engineering alloys, ranging from the aerospace grade aluminium alloys 2024 and 7075 to stainless steels, are vulnerable to localised corrosive degradation under certain environmental conditions.

The local nature of corrosion is most of the time dictated by the intrinsic features of the microstructure. The intermetallic second phases in age-hardened aluminium alloys, for example, are known to act as nucleation points for local corrosive attack [1]. Similarly, pitting corrosion in stainless steels was found to initiate in the vicinity of MnS inclusions [2]. Furthermore, the time-dependent evolution and further propagation of corrosive events depends on the local changes in chemistry of the microstructure [3-4], which will ultimately determine the mechanism and rate of such propagation.

For these reasons, characterising and, consequently, understanding the degradation mechanism of these alloys is not only complex, but must also rely on in-situ and highly spatio-temporally resolved techniques [5].

In this contribution, we present a recently developed spectro-electrochemical scanning flow cell, which enables to study corrosive degradation phenomena, as well as corrosion prevention with the use of corrosion inhibitors. Such scanning flow cell allows to induce local corrosion by electrochemically controlling the polarization of the working electrode immersed in 10 mM NaCl solution. Simultaneously, we can characterize the time-dependent appearance of micro- to macroscopic surface features by means of in-situ optical microscopy. This information can be further supported by the online identification and quantification of dissolved mass currents by means of online inductively coupled plasma mass spectrometry (ICP-MS). The combination of this techniques allows us to estimate not only the typical surface-initiated corrosion mechanisms, but also the characteristic corrosion rates of different metal alloys.

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[5]M. Olgiati *et al.*, *Corrosion Science***192,** 109836 (2021)

CA-TuP-2 Diamond Hydrogenation Using a Compact and Cost-Effective Low–Power Plasma*, **J. Trey Diulus**,* NIST Center for Nanoscale Science and Technology*; F. Yi,* NIST-Gaithersburg*; E. Strelcov,* NIST Center for Nanoscale Science and Technology*; D. LaVan,* NIST-Gaithersburg*; A. Kolmakov,* NIST Center for Nanoscale Science and Technology

Device fabrication of field effect transistors (FET)s and other electronic devices are still largely dependent on silicon, which has been the core semiconductor material for over seven decades.[1,2] Newer materials, like SiC and GaN, offer wide-bandgap alternatives to silicon that are required for high power electronics with improved carrier mobility, carrier density, and high operation temperatures.[2,3] Alternatively, diamond is another promising semiconductor material, with its ultra-wide bandgap (5.5 eV), unmatched thermal conductivity, breakdown voltage, and high charge carrier mobility (~4000 $cm^2 V^{-1} s^{-1}$).[3] Recently, advances in diamond growth through techniques like chemical vapor deposition (CVD) have demonstrated wafer size of diamond single crystals,[4] overcoming the primary challenge towards industrial implementation. However, hydrogenation of the diamond surface is a necessary process to fabricate high-mobility diamond FETs. The H-terminated surface, however, is sensitive to ambient adsorbates that deteriorate the stability of surface conductivity when using modern device manufacturing processes. The present method for H-terminating a diamond surface is via a high-power (> 1 kW) microwave plasma that typically utilizes a specially designed chamber for high pressure (tens of kPa) exposures at elevated temperatures (>700 °C).[5] Due to the high cost required for such a system, a roadblock exists that prevents broader research community efforts for diamond related devices that is imperative for improving high-power/frequency electronics. Thus, we have developed a recipe for H-terminating diamond based on an H_2 plasma generated by a simple low-power (75 W), low pressure (tens of Pa) RF plasma cleaner for a cost-effective diamond hydrogenation method. Furthermore, we have developed a relevant plasma characterization metrology for H-termination by real time monitoring of the radical flux using catalytically activated and reference metal film samples loaded in a nano-calorimeter,[6] in conjunction with standard optical spectroscopy. We have tested our hydrogenation method on diamond samples by characterizing the surface before and after plasma treatment with *in situ* x-ray photoelectron spectroscopy and *ex situ* 4–point probe measurements. Our efforts will provide researchers a facile route towards diamond research and will broaden the diamond research community.

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CA-TuP-3 A Study of the D-Parameter: Evaluating Measurement Techniques in X-ray Photoelectron Spectroscopy (XPS)*, **Alvaro Lizarbe**, G. Major, B. Clark,* Brigham Young University*; D. Morgan,* Cardiff University*; M. Linford,* Brigham Young University

When looking at carbonaceous material analysis, the D-parameter plays a pivotal role in determining the sp^2/sp^3 ratio via X-ray photoelectron spectroscopy (XPS). Despite its utility, the methodological inconsistency in generating the peak envelope introduces uncertainty in the D-parameter analysis. This study investigates two distinct approaches to measuring the D-parameter, a modified b-spline method and a polynomial regression line fit. The b-spline method entails the creation of synthetic Gaussian peaks in the carbon KLL Auger peak, maintaining a consistent full width at half maximum (FWHM) and equal distance apart but varying areas. The polynomial regression approach, on the other hand, fits the curve by manipulating the degree of the polynomials. Both techniques strive to generate a fit that mirrors the raw data as closely as possible, thereby facilitating a more precise derivative from which the D-parameter can be computed. To evaluate the efficacy of these methods, a comparative analysis was conducted using different carbonaceous materials such as direct current chemical vapor deposition (DC-CVD) diamonds, carbon nanotubes, and highly oriented pyrolytic graphite (HOPG). The results are compared against the traditional D-parameter values for these materials. This research not only contributes to improving the reliability and reproducibility of D-parameter measurements but also offers valuable insights into the optimization of envelope creation methods in XPS.

CA-TuP-4 Proton and Hydroxide Diffusion Within Supercooled Water*, **Megan Dunlap**,* Pacific Northwest National Lab*; L. Kringle, R. Smith, B. Kay, G. Kimmel,* Pacific Northwest National Laboratory

The molecular mechanisms for the diffusion of protons and hydroxides within liquid water are controversial. To elucidate these processes, we examine proton and hydroxide diffusion within water films under ultra-high vacuum that are heated to temperatures spanning 110-140 K. At these temperatures, the water molecules are arrested, but the charged species move rapidly through the ~40 nm thick films. Their progress is monitored with reflection absorption infrared spectroscopy (RAIRS) via the exchange of the ion with isolated D_2O ‘probe’ molecules within the film to form HDO. We have investigated the exchange rate as a function of the distance that the ions must travel to reach the D_2O, the temperature, the total thickness of the film, and the ion type. Based on the temporal evolution of the D_2O, we have found that both diffusion and trapping of the ion within the film are required to describe the observations.

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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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.

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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.

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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.

Sandia National Laboratories is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.

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$^{\text{TM}}$ 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].

[1] M. K. Passarelli *et al.*, “The 3D OrbiSIMS—label-free metabolic imaging with subcellular lateral resolution and high mass-resolving power,” *Nat. Methods*, no. november, p. nmeth.4504, 2017, doi: 10.1038/nmeth.4504.

[2] L. Matjacic *et al.*, “OrbiSIMS metrology part I: Optimisation of the target potential and collision cell pressure,” *Surf. Interface Anal.*, no. November 2021, pp. 1–10, 2021, doi: 10.1002/sia.7058.

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

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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This work was partially financed by CONACyT Project Fronteras 58518, Mexico.

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[2] A. Herrera-Gomez, Interchannel Coupling with Valence Band Losses as the physical origin of the Shirley background in photoemission spectra (Old title: The unresolved physical origin of the Shirley background in photoemission spectra), Queretaro, 2015. http://www.qro.cinvestav.mx/%0A~aherrera/reportesInternos/unknownOriginShirley.pdf.

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.

[1] Werner, W. , Smekal, W. , Powell, C. and Gorham, J. (2021), Simulation of Electron Spectra for Surface Analysis (SESSA) Version 2.2 User's Guide, Natl Std. Ref. Data Series (NIST NSRDS), https://doi.org/10.6028/NIST.NSRDS.100-2021.

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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[2] K. S. Egorova, E. G. Gordeev, and V. P. Ananikov, *Chem. Rev.* **117**, 7132 (2017).

[3] E. F. Smith, I. J. Villar Garcia, D. Briggs et al., *Chem. Commun.* **45**, 5633 (2005).

[4] B.P. Reed, J. Radnik, and A.G. Shard, *Surf. Sci. Spectra***29**, 014001 (2022).

[5] X. Knigge and J. Radnik, *Surf. Sci. Spectra***30**, 014006 (2023).

[6] M. P. Seah, I. S. Gilmore, and S. J. Spencer, *Surf. Sci.* **461**, 1 (2000).

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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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.

CHIPS Act Mini-Symposium
Room C120-122 - Session CPS+CA-WeA

CHIPS Act: Interfaces and Defects

Moderators: Tina Kaarsberg, U.S. Department of Energy, Advanced Manufacturing Office, **Andrei Kolmakov**, National Institute of Standards and Technology (NIST)

2:20pm **CPS+CA-WeA-1 Future Needs and Current Trends in Interfacial Metrology for the Development of Reliable Ultra-Wide Bandgap Electronics***, **Luke Yates**, A. Jarzembski, W. Hodges, M. Bahr, W. Delmas, Z. Piontkowski, A. McDonald, M. Smith, B. Rummel, C. Glaser, A. Binder, J. Steinfeldt, A. Allerman, A. Armstrong, B. Klein, G. Pickrell,* Sandia National Laboratories*; D. Morisette,* Purdue University*; J. Cooper,* Sonrisa Research Inc.*; R. Kaplar,* Sandia National Laboratories **INVITED**

Recent advancements in epitaxial growth and substrate development continue to inspire the next generation of wide-bandgap (WBG) semiconductor devices. In the last decade, the silicon carbide (SiC) and gallium nitride (GaN) material systems have seen extraordinary advancements that allow an increased commercial device adaptation. However, there still exists many reliability concerns that directly impact device manufacturing. These concerns manifest in our inability to accurately quantify and mitigate interface charge effects and material defects that exist within device structures due to growth conditions and processing limitations. Commercial endeavors will continue to address such concerns for WBG devices, but it is crucial that the research community complements and promotes these efforts through advanced interfacial metrology methods that can be applied to both current WBG devices and future ultra-wide-bandgap (UWBG, $E_g > 3.4eV$) materials and devices, thus enabling the next leap forward in electronic device performance. These include materials such as high-Al-content AlGaN/AlN, Ga_2O_3, cubic BN, diamond, and others. Due to device performance scaling approximately as E_g^6, there exists substantial potential that has yet to be fully embraced in UWBG devices.

Interfacial metrology is a broad topic area that encompasses numerous thermal, mechanical, chemical, optical, and electronic properties at (dis)similar material interfaces. It is inextricably linked to our ability to develop devices that fully exploit the electronic capabilities of a given material system. This talk discusses current optical, acoustic, and electrical characterization efforts at Sandia and within the broader community to visualize and quantify interfacial properties, defects, and undesirable electronic charges within (U)WBG materials and devices. Specifically, a coupled hyper-spectral frequency-domain thermoreflectance/laser doppler vibrometry (FDTR/LDV) system that allows for enhanced understanding of thermal/mechanical properties of buried interfaces with a sensing depth greater than standard FDTR approaches has been implemented. Additionally, an improved quasi-static capacitance analysis method has been developed to more accurately evaluate interface traps at dielectric/(U)WBG material interfaces. Direct optical and photoemission approaches are becoming increasingly difficult to effectively utilize as larger bandgap devices are developed, necessitating the need for advanced thermal, vibrational, and electronic analysis methods. Future interfacial metrology efforts will require non-destructive methods that are capable of highly resolved in-situ full-field monitoring of buried interfaces within a device.

SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525

3:00pm **CPS+CA-WeA-3 Diamond/h-BN Heterostructures for High-Performance Electronics***, **Yamaguchi Takahide,*** National Institute for Materials Science, Japan **INVITED**

Diamond is an ultra-wide bandgap semiconductor displaying a high breakdown electric field, high thermal conductivity, and high carrier mobilities. These intrinsic properties are suitable for creating power conversion and communications devices. In order to utilize its full potential, however, the properties of its surfaces and interfaces to other materials used in combination are important. Hydrogen-terminated diamonds (diamonds with their surface carbon atoms covalently bonded with hydrogen atoms) are widely used to make field-effect transistors (FETs). They show p-type surface conductivity even when the diamonds are not doped intentionally. The surface conductivity is attributed to surface transfer doping; electrons in the valence band of diamond are transferred to acceptors in an adjacent coating material, thereby forming holes in the diamond surface. The acceptor material includes adsorbed water, NO_2 gas, and oxides such as Al_2O_3, MoO_3, and V_2O_5, and coating the diamond surface with an acceptor material has been thought to be necessary to generate the surface conductivity. However, the surface transfer doping is accompanied by negatively charged acceptors, which cause carrier scattering and reduce hole mobility. It also leads to normally-ON operation, a finite conductivity at zero gate bias, which is undesirable particularly in power electronics.

In this presentation, I will present current trends in diamond electronics and our recent work on the creation of high-performance hydrogen-terminated diamond FETs without surface transfer doping [1]. We transferred a cleaved single crystal of hexagonal boron nitride (h-BN) on hydrogen-terminated diamond and used it as a gate insulator. This is useful for avoiding the formation of defects, which occurs in conventional deposition techniques and can cause acceptor states [2]. In addition, the transfer was made without exposing the diamond surface to air, using a vacuum suitcase and an Ar-filled glove box, which reduced the density of atmospheric acceptors. Our FETs exhibited excellent ON-state characteristics such as a room-temperature mobility of 680 $cm^2V^{-1}s^{-1}$, sheet resistance of 1.4 kΩ and gate-length-normalized ON current of 1600 µm mA mm^{-1}. These are among the best among p-channel wide-bandgap FETs. The FETs also exhibited normally OFF behavior with an ON/OFF ratio of 10^8. Our new approach for making diamond FETs could lead to the development of high-performance wide-bandgap p-channel devices for power electronics and communications.

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4:20pm **CPS+CA-WeA-7 Hydrogenation of a $Cu_{2-x}O$ Confined Under Hexagonal Boron Nitride***, **J. Trey Diulus**, E. Strelcov,* NIST Center for Nanoscale Science and Technology*; Z. Novotny,* Empa (Swiss Federal Laboratories for Materials Science and Technology), Switzerland*; N. Comini,* University of Zurich, Switzerland*; A. Naclerio, P. Kidambi,* Vanderbilt University*; J. Osterwalder,* University of Zurich*; A. Kolmakov,* NIST Center for Nanoscale Science and Technology

Hexagonal boron nitride (h-BN) exhibits a wide array of unique chemical and electrical properties that presents itself useful in numerous applications, such as a gate dielectric for high mobility diamond transistors,[1] increasing corrosion resistance,[2] or a device encapsulating material.[3] h-BN can be epitaxially grown by chemical vapor deposition (CVD) on copper surfaces with any orientation, and a near perfect lattice match on the Cu(111) surface, making Cu an ideal substrate to study intercalation.[4,5] Intercalation of O_2 through h-BN to monitor oxidation of the Cu substrate can be studied during exposure to near ambient oxygen partial pressures (1-100 Pa),[6] or following exposure to atmosphere.[5] The oxidation occurs predominately at defects and/or grain boundaries in the h-BN, and occurs even at room temperature if the pressure is high enough (atm pressure), leading to a lifetime of a few weeks at these conditions for use of pristine unoxidized h-BN/Cu heterostructures.[5] To better understand this intercalation behavior, we studied the intercalation of H_2 to observe the extent of recovery of the original metallic surface/interface after the h–BN/$Cu_{2-x}O$ interface is formed. Using polycrystalline Cu foils with CVD grown h-BN after exposure to atmosphere for ~1 month as a model system, we assessed the reduction of the surface via two hydrogenation methods: (i) simple H_2 exposure of 10 Pa followed by annealing in vacuum (sequentially) and during H_2 exposure (simultaneously) (ii) exposure to a low power (75 W) H_2 remote plasma also using 10 Pa, allowing for H radicals to interact with the surface. With *in situ* x-ray photoelectron (XPS) and Auger electron spectroscopy (AES), we track the changes in surface chemistry following each hydrogenation attempt. Additionally, *in situ* scanning electron microscopy provides morphological maps of the foil surface. To further study this hydrogenation mechanism from a fundamental perspective, we utilized h-BN grown on single crystalline Cu(111) and collected *in situ* ambient pressure XPS for the reduction of an ordered cuprous oxide confined beneath h-BN. Ultimately, H-radicals and ions can attack the confined oxide and partially reduce the surface, yet we were unable to fully recover metallic Cu. Our results indicate the original metallic interface might be repaired without damaging the overlaying h-BN, which is of practical importance for development of h-BN encapsulated devices and interfaces.

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[6] Diulus, J. T. *et al.* Towards 2D-confined catalysis on oxide surfaces. *ACS Nano* **Submitted** (2023)

4:40pm **CPS+CA-WeA-8 A Proven Model for Workforce Development***, **David Ruzic**, D. Andruczyk,* University of Illinois at Urbana-Champaign

At the University of Illinois at Urbana-Champaign we have set up two complimentary structures to enable workforce development in the field of semiconductor manufacturing. The first is a relatively new degree program, a "Masters of Engineering in Plasma Engineering". This is a non-thesis master's degree which specializes in plasma technology and science related to making the machines which make the chips. The flagship class is a plasma laboratory where the students operate and analyze the experiments themselves in Vacuum Technology, DC Plasmas, RF Plasmas, Langmuir Probes, Spectroscopy, Plasma Etching, Plasma PVD Deposition, Atmospheric Pressure Plasmas and Fusion Plasmas. The program can usually be finished in three semesters and is open to students from all fields of engineering and science.

This program can be coupled with sponsored research at the University, particularly through the Illinois Plasma Institute. Companies who are sponsoring research at Illinois can use the Masters program to recruit, retain or re-train employees. In the case of a current employee, that person goes to Illinois while still working for the company, perhaps being paid less than 100%. Their work role at Illinois is to help work on the research project that in being sponsored, and do other remote work. Their school role is to take the courses in the degree program which includes classes directly related to their work for the company itself. If the company pays for the tuition, the student is required to continue working for the company upon graduation for a limited time, or pay back the tuition. The company is ensured a better-trained more-educated employee. The student is ensured of a job.

Examples will be described, and a program outlined that could be set-up at any major University.

5:00pm **CPS+CA-WeA-9 Characterization of Buffer Layers for Remote Plasma-Enhanced Chemical Vapor Deposition of Germanium-Tin Epitaxial Layers***, **Bridget Rogers,*** Vanderbilt University*; S. Zollner, C. Armenta,* New Mexico State University*; G. Grzybowski,* KBR*; B. Claflin,* Air Force Research Lab

Germanium-tin alloys are of interest for infrared light detectors and lasers to increase capabilities in image and data capture and transmission, because they can have a direct band gap with more than about 7% tin. Remote plasma-enhanced chemical vapor deposition (PE-CVD) is particularly attractive for growth of Ge-Sn alloys because it enables low-temperature epitaxy directly on Si using common precursors GeH_4 and $SnCl_4$. The growth of such epilayers can be optimized with an initial high-temperature buffer layer. This presentation will focus on the characterization of this buffer layer using atomic force microscopy, ellipsometry, thin-film powder x-ray diffraction, and x-ray photoelectron spectroscopy (XPS) for different growth conditions.

Thin Ge and Ge-Sn buffer layers with 10-20 nm thickness were deposited on Si (100) substrates for one minute at temperatures from 360°C to 500°C varying the $SnCl_4$ flow. Ellipsometry spectra for all films show critical point structures in the E--$_1$, $E_1+\Delta_1$, and E_2 region of Ge, indicating that all layers are crystalline. A layer grown at 360°C without $SnCl_4$ is well described as an 11 nm thick layer of crystalline germanium with 2 nm of roughness. Adding $SnCl_4$ to the gas flow significantly reduces the height of the ε_2 maximum at E_2, indicating that the layer is rough. In addition, a new broad peak appears near 1.3 eV, which is attributed to plasmonic effects arising from metallic β-tin inclusions. The plasmon peak disappears in the layers grown at 490°C with the same $SnCl_4$ flow. We conclude that depositing the buffer layer with $SnCl_4$ at low temperatures leads to β-Sn precipitates, where plasmon oscillations can be excited, which are not present for high-temperature growth.

The tin contents in the layers were also estimated by x-ray photoelectron spectroscopy. While XPS measures the total amount of tin in the layers, the presence of substitutional tin in $Ge_{1-x}Sn_x$ alloy buffers is best determined with x-ray diffraction. The (002) diffraction peak is absent in our buffers grown without $SnCl_4$ or at high temperature. The (004) XRD peak position in these layers is also very similar to pure Ge. The $Ge_{1-x}Sn_x$ (002) peak does appear in buffers grown at temperatures lower than 460°C. From the position of the (004) XRD peak, we estimate the tin content to be below 7%. Tin content determined from XRD shifts is much lower than the total tin content of about 20% estimated by XPS.

In summary, the substitutional tin content in thin $Ge_{1-x}Sn_x$ buffer layers grown by PE-CVD is modulated by temperature and $SnCl_4$ flow rates. Excess tin is present in β-tin precipitates, which lead to plasmonic resonances in ellipsometry spectra.

5:20pm **CPS+CA-WeA-10 Comparative Study of Mechanical and Corrosion Behaviors on Heat Treated Steel Alloys***, **Moe Rabea**,* California State Polytechnic University, Pomona

This research examines the effects of heat treatment processes on the mechanical properties and corrosion resistance of 1045 and 4140 Steel Alloys for industrial applications. Heat treatment processes of full annealing, normalizing, quenching, and tempering are carried out on the alloy samples. The mechanical and corrosion resistance tests of the heat treated samples are carried out and the results obtained are related to their morphologies analysis. The results show that the heat treatment processes have an effect on the tensile strength, impact, and a significant effect on the corrosion resistance of the alloy samples. With respect to the strain characteristics, significant improvement in the ductility of the samples is recorded in the full annealing and alloy tempered samples. Thus, for application requiring strength and ductility such as in aerospace industries, this tempered heat treated alloy could be used. In addition, the quenched sample shows a significant improvement in hardness.

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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2. M R. Keenan, G. F. Trindade, A. Pirkl, C. L. Newell, K. Ayzikov, J. Zhang, L. Matjacic, H. Arlinghaus, A. Eyres, R. Havelund, J. Bunch, A. P. Gould, A. Makarov and Ian S. Gilmore, in preparation.
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

[1]R. Sandenbergh, M. Biermann, and T. von Moltke, 'Surface Analytical Characterization of Chromium Passivation on Tinplate', in *Passivation of Metals and Semiconductors, and Properties of Thin Oxide Layers*, P. Marcus and V. Maurice, Eds., Amsterdam: Elsevier Science, 2006, pp. 143–148. doi: 10.1016/B978-044452224-5/50024-X.

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[3]M. d'Halluin *et al.*, 'Graphite-supported ultra-small copper nanoparticles – Preparation, characterization and catalysis applications', *Carbon*, vol. 93, pp. 974–983, Nov. 2015, doi: 10.1016/j.carbon.2015.06.017.

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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.

[1] D R Baer et al, J. Vac. Sci. Technol. A 39, 021601 (2021); https://doi.org/10.1116/6.0000873

[2] G. H. Major et al, J. Vac. Sci. Technol. A 38, 061204 (2020); https://doi.org/10.1116/6.0000685

[3] G. H. Major et al, J. Vac. Sci. Technol. A 38, 061203 (2020) https://doi.org/10.1116/6.0000377

[4] D R Baer and M. H. Engelhard, Journal of Surface Analysis Vol. 26, No.2 (2019) pp. 94-95.

[5] D R Baer, J F Watts, A Herrera-Gomez, K J Gaskell, Surf Interface Anal. 2023; 1- 9. doi:10.1002/sia.7194

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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[2] E.W.B. Dias et al. Phys Rev B 78(2), 4553–4556 (1997).

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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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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).

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[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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