

Applied Surface Science Room 117 - Session AS-TuA

Theory, Surface Structure and Processes

Moderators: Paul S. Bagus, University of North Texas, Jodi Grzeskowiak, Tokyo Electron America, USA

2:15pm AS-TuA-1 Advances in Understanding Structure and Electron Transfer Dynamics at Iron Oxide/Water Interfaces, *Kevin Rosso*, Pacific Northwest National Laboratory

INVITED
Structure and dynamics at iron oxide/water interfaces, which govern rates of adsorption, electron transfer, growth/dissolution, have long been challenging to accurately simulate because of the prominent role of iron cation valence on acidity and ligand exchange behavior, and unique electronic structure considerations in the solid state. Iron oxides are wide band gap semiconductors with a narrow conduction band arising from strongly localized 3d orbitals. Consequently, charge carriers tend to self-trap as polarons whose mobilities are controlled by thermally activated site-to-site hopping. Proper theoretical description of such properties requires thoughtful trade-off's between necessary accuracy versus efficiency.

I will provide a decadal perspective on computational efforts applied to processes at hematite/water interfaces, highlighting the importance of steady methodological improvements. The talk will feature 1) how water organizes and is dynamically stabilized at distinct hematite facets, 2) the structure and hopping kinetics of electron and hole polarons, and 3) the free energies of ferrous iron adsorption and valence interchange electron transfer with the surface. It will be shown that ab initio molecular dynamics is now both a viable and essential tool for accurately determining the H-bonding network of adsorbed water and the acidity constants of surface hydroxo groups, while static density functional theory is still a useful tool for water binding energetics. Gap-optimized hybrid functionals show that while the hole polaron generally localizes onto a single iron site, its mobility is limited by the tetragonal distortion it induces, whereas the electron polaron induces a smaller distortion resulting in delocalization over two neighboring Fe units and a factor of three higher mobility. Finally, for computationally intensive processes such as ferrous iron adsorption, it will be shown that use of neural network potentials such as the Behler-Parrinello type is a promising alternative to classically parameterized molecular dynamics, offering both the precision of first principles calculations and the same order of computational efficiency to that of classical simulations. The collective findings bode well for ultimately enabling a robust basis for interpretation of experimental observables near the atomic-scale including complex multi-step processes such as redox-catalyzed dissolution and growth.

2:45pm AS-TuA-3 Manifestation of Correlated Electronic Structure in a Kagome Metal YbTi_3Bi_4 , *Anup Pradhan Sakhya*, University of Central Florida; *B. Ortiz*, Materials Science and Technology Division, Oak Ridge National Laboratory; *B. Ghosh*, Northeastern University, US; *M. Sprague, M. Mondal*, University of Central Florida; *M. Matzelle*, Northeastern University, US; *I. Elius, N. Valadez*, University of Central Florida; *D. Mandrus*, University of Tennessee Knoxville; *A. Bansil*, Northeastern University, US; *M. Neupane*, University of Central Florida

Kagome lattices have emerged as an ideal platform for exploring various exotic quantum phenomena such as correlated topological phases, frustrated lattice geometry, unconventional charge density wave orders, Chern quantum phases, superconductivity, etc. Here, we report the discovery of a new Ti-based kagome metal YbTi_3Bi_4 which is characterized using angle-resolved photoemission spectroscopy (ARPES) and magnetotransport, in combination with density functional theory calculations. Our ARPES results reveal the complex fermiology of this system along with the spectroscopic evidence of four flat bands. Furthermore, our electronic structure measurements show the presence of multiple van Hove singularities originating from Ti 3d orbitals. We have identified that the system exhibits topological nontriviality with surface Dirac cones at the Γ point and a bulk linearly dispersing gapped Dirac-like state at the K point as indicated by our theoretical calculations. These results establish YbTi_3Bi_4 as a novel platform for exploring the intersection of nontrivial topology, and electron correlation effects in the wider LnTi_3Bi_4 (Ln = lanthanide) family of materials.

3:00pm AS-TuA-4 Impact of Surface Pretreatment on $\text{Al}_2\text{O}_3/\text{GaN}$ and HfO_2/GaN Band Offsets Measured by X-Ray Photoelectron Spectroscopy, *Melissa Meyerson, P. Dickens, J. Klesko, B. Rummel, P. Kotula, A. Binder*, Sandia National Laboratories

The need for modern power devices with lower ON-resistances, higher breakdowns, and improved efficiencies is increasing as power demands in electronics continue to rise. Gallium nitride (GaN) has emerged as a promising candidate to satisfy these demands due to its advantageous material properties as a wide bandgap semiconductor (e.g., high breakdown electric field, enhanced mobility, and a high saturation velocity). The use of GaN in power electronics often relies on the interactions between the GaN and a dielectric layer, such as Al_2O_3 , which are highly dependent on the properties of the materials at the interface. Variations in the band offset and interface trap state densities can be impacted by a variety of processing factors, including the surface chemistry of the GaN prior to dielectric deposition. Since the surface chemistry of the GaN is affected by the methods used to clean the surface prior to deposition of the dielectric, it is expected that these interfacial properties will also be affected by the cleaning method used. Here, we study the interfacial properties of $\text{Al}_2\text{O}_3/\text{GaN}$ and HfO_2/GaN films using X-ray photoelectron spectroscopy (XPS) to measure the band offsets as a function of GaN cleaning method. Additionally, a Ga_xO_y interlayer has been identified at this interface by XPS, which is correlated with interface trap state densities measured from capacitance-voltage measurements of subsequently fabricated MOS-capacitors.

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3:15pm AS-TuA-5 Absence of Electronic Structure Reconfiguration in EuSnP Across the Antiferromagnetic Transition, *Milo Sprague, A. Sakhya*, University of Central Florida; *S. Regmi*, Idaho National Laboratory; *M. Mondal, I. Bin Elius, N. Valadez*, University of Central Florida; *T. Romanova, A. Ptok, D. Kaczorowski*, Polish Academy of Sciences, Poland; *M. Neupane*, University of Central Florida

Magnetic ordering in lanthanide-based metals is commonly attributed to RKKY interactions, where localized magnetic f electrons interact magnetically with itinerant conduction electrons through exchange interactions. Due to the intricate interplay between the electronic band structure and magnetic ordering, many lanthanide magnetic metals undergo significant changes in their electronic spectrum. In our study of the europium-based antiferromagnetic metal EuSnP , employing angle-resolved photoemission spectroscopy (ARPES) and first-principles density functional theory (DFT) calculations, we surprisingly found no modifications to the band structure upon cooling below the paramagnetic to antiferromagnetic transition temperature. We discuss potential reasons for this absence of observed reconstruction in this compound.

4:00pm AS-TuA-8 Calculation of X-Ray Absorption Spectra of f-Element Compounds from First Principles, *Jochen Autschbach*, University at Buffalo, SUNY

INVITED
This talk will be concerned with calculations of X-ray absorption near-edge structure (XANES) spectra for f-element compounds using multi-configurational wavefunction methods (using complete and restricted active space self-consistent field (CAS/RASSCF) methods and variants thereof), along with supporting density functional calculations. A focus of our research has been the connection of the observed spectral features and the underlying covalent bonding in the systems, in particular, the involvement of the valence f-shells of lanthanides and actinides. The talk will cover published studies of actinyl(VI) species, actinide hexa-chlorides, cerocene vs. CeO_2 , as well as on-going research on a variety of Ce(IV) materials.

Selected relevant references:

- [1] Sergentu, D.-C.; Autschbach, J., 'Covalency in Actinide(IV) Hexachlorides in Relation to Chlorine K-Edge X-ray Absorption Structure', *Chem. Sci.* 2022, 13, 3194–3207. <https://doi.org/10.1039/D1SC06454A>
- [2] Sergentu, D.-C.; Autschbach, J., 'X-ray absorption spectra of f-element complexes: Insight from relativistic multiconfigurational wavefunction theory', *Dalton Trans.* 2022, 51, 1754–1764. <https://doi.org/10.1039/d1dt04075h>

[3] Sergentu, D.-C.; Booth, C. H.; Autschbach, J., 'Probing multicongfigurational states by spectroscopy: The cerium XAS L₃-edge puzzle', Chem. Eur. J. 2021, 27, 7239–7251. <https://doi.org/10.1002/chem.202100145>

4:30pm **AS-TuA-10 The XPS of Ni Compounds – A Comparative Study**, *Paul S. Bagus*, University of North Texas; *C. Nelin*, Consultant; *N. Lahiri*, Pacific Northwest National Lab; *E. Ilton*, Pacific Northwest National Lab

The Ni 2p XPS of the ionic compounds NiO, Ni(OH)₂, and Ni(CO)₃ are analyzed, interpreted, compared with each other and, as well, the theoretical results are compared with XPS measurements. The main features as well as the satellite, shake, features are considered. The theoretical analysis is based on the properties of ab initio molecular orbital wavefunctions, WFs, for cluster models of the compounds. We distinguish two theoretical approaches. The first is where only the angular momentum coupling of the core 2p open shell and the valence open shell which contains 8 dominantly Ni 3d orbitals is considered to form the ionic wavefunctions, WFs. The second is where excitations from closed shell orbitals into the valence open shell space is added. The second approach properly describes the XPS satellites and puts, for the first time, the concept of "charge transfer" in the core ionic states on a firm theoretical basis. It is important to choose orbitals and WFs which allow the mixing of normal and shake character and novel methods are used to characterize the orbitals and to describe the WF character. The consequences for the XPS of the variation of the Ni-ligand distance are examined. Three key results are: (1) The extended theoretical approach must be used to describe the satellites and it also somewhat modifies the main XPS peaks. (2) The choice of orbitals is critical to properly describe the XPS, especially the satellites, and this can be related to the electronic structure of the excited states. The differences between the XPS of the different compounds are mainly for the satellite features and the reasons for this are explained.

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4:45pm **AS-TuA-11 The Experimental Asymmetry of the 2p, 3d, and 4f, Photoemission Spectra of the Elements of the 3rd, 4th, and 5th Periods**, *Alberto Herrera-Gomez*, Cinvestav, Mexico; *A. Dutoi*, University of the Pacific; *D. Guzman-Bucio*, CINVESTAV-Queretaro, Mexico; *D. Cabrera-German*, Universidad de Sonora, Mexico; *A. Carmona-Carmona*, Benemerita Universidad Autonoma de Puebla, Mexico; *O. Cortazar-Martinez*, CINVESTAV-Unidad Queretaro, Mexico; *B. Crist*, The XPS Library; *M. Mayorga-Garay*, CINVESTAV-Unidad Queretaro, Mexico

We carried out a peak-fitting analysis of the 2p, 3d, and 4f, spectra of the elements of the 3rd, 4th, and 5th periods, respectively. We found that the Double-Lorentzian lineshape (DL) [1] closely reproduces the asymmetry in all cases. Moreover, the DL asymmetry shows clear trends with atomic-number. This contrasts with the Doniach-Sunjic lineshape, which, in most cases, does not reproduce the experimental data; besides, it cannot be used in quantitative studies because it is not integrable.

The asymmetry parameter (a_{DL}) for the 2p_{3/2} photoemission line shows a decreasing trend with increasing atomic number, with a pronounced shoulder in the region of the ferromagnetic metals. For the 2p_{1/2} photoemission line, the DL asymmetry increases for the ferromagnetic metal. This indicates a relationship between the asymmetry and the electronic structure of the metals.

a_{DL} also shows interesting tendencies for the 3d photoemission spectra of the 5th-period elements from Rb to In. There is a significant difference in the DL parameter between the two 3d branches for elements with an empty 4d band (Rb and Sr). a_{DL} is lower for the elements with a half-filled (Mo [Kr]5s¹4d⁵), almost filled (Ru [Kr]5s¹4d⁷ and Rh [Kr]5s¹4d⁸) and filled 4d band (Ag [Kr]5s¹4d¹⁰, Cd [Kr]5s²4d¹⁰, and In [Kr]5s²5p¹). These results suggest that the asymmetry is related to the 4d valence electrons.

A theoretical approach is proposed.

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[1] A. Herrera-Gomez, D.M. Guzman-Bucio, A.J. Carmona-Carmona, O. Cortazar-Martinez, M. Mayorga-Garay, D. Cabrera-German, C.A. Ospina-Ocampo, B.V. Crist, J. Raboño-Borbolla, Double Lorentzian lineshape for asymmetric peaks in photoelectron spectroscopy, Journal of Vacuum Science & Technology A 41 (2023). <https://doi.org/10.1116/6.0002602>.

5:00pm **AS-TuA-12 Computational Exploration of Dimension Limits for Narrow Gap Transport of Reactive Species**, *Greg Hartmann*, *S. Sridhar*, *P. Ventzek*, Tokyo Electron America, Inc.

State of the art device fabrication is pushing the limits of etch processes in terms of achievable critical dimensions. Passing these limits requires an insight into the fundamentals of dry etch processes, i.e. fluxes of radicals and ions reaching the etch front and how they are transported into the feature. Here we discuss the 'in-feature' transport of radicals for narrow trenches beyond the limits of the conventional perspective of Knudsen diffusion. Advances in computational techniques, particularly density functional theory (DFT), enable theoretical models on the scale of a few molecular diameters to elucidate transport processes on the atomic scale. Van-der-Waals corrected DFT predicts significant intermolecular interactions provide a severely-constricted transport regime where a diffusing species is always interacting with at least one wall; surface diffusion has been identified as significant within typical process dimensions but may be the dominant mode of transport under this condition. Cessation of transport is predicted at the transition to solid-state diffusion. Multiphysics models utilizing kinetic data predicted via DFT predict a critical depth under which radical or by-product transmission is limited; the radical-starved limit is predicted to occur on the order of hundreds of nanometers. Consequently, a range of critical dimensions are predicted to create an inherently radical-starved condition. Scaling relationships provide insight into critical dimension limits across varied material selection.

5:15pm **AS-TuA-13 High-Temperature Diffraction and Surface Electron-Phonon Coupling of the Unreconstructed Metallic and (3x1)-O Reconstructed Nb(100) Surfaces by Helium Atom Scattering**, *Michael Van Duinen*, *C. Thompson*, University of Chicago; *M. Kelley*, *C. Mendez*, Cornell University; *S. Willson*, *V. Do*, University of Chicago; *T. Arias*, Cornell University; *S. Sibener*, University of Chicago

Superconducting radio frequency (SRF) cavities are the fundamental accelerating components of linear particle accelerators. Niobium is the material of choice for SRF cavities due to its high malleability, thermal conductivity, and superconducting critical temperature (T_c). Despite Nb having a T_c of ~9 K, the practical operating temperature of a Nb SRF cavity is ~2 K, below the boiling point of He and consequently quite expensive to operate. The improvement of Nb SRF cavities and the lowering of operating costs has been focused primarily on the development of new materials on the Nb surface. Due to the ~100 nm superconducting penetration depth of Nb, only ~1 micron of material need be deposited onto the Nb surface to completely change its superconducting properties. One of the primary limitations to both Nb SRF cavities and the new materials under study is the presence of a thermally stable and robust oxide. Understanding the formation, stability, and dynamics of the oxide and its effects on the operation of Nb SRF cavities requires study both of material superconducting properties and atomic-scale surface material chemistry. Helium atom scattering (HAS) is a surface diffraction technique that has the ability to probe surface structure, bonding, and dynamics. The chemically inert He and an ultra-high vacuum (UHV) environment make HAS an ideal probe for the chemically reactive and sensitive Nb surface. Furthermore, experts in the field have developed theory involving the He-electron interaction and the surface electron-phonon interaction to formulate an equation by which HAS data can be used to determine an electron-phonon coupling (EPC) constant (λ) for the surface (λ_s). These data can then be used to find surface analogues for T_c along with other superconducting properties relevant to SRF cavity operation. We study the Nb(100) surface for its recognizable and stable (3x1)-O NbO oxide reconstruction. We find a λ_s of 0.50 ± 0.08 for the metallic Nb(100) versus a bulk λ of ~1, demonstrating that the superconducting state is significantly modified at the surface. We also find a λ_s of 0.20 ± 0.06 for the (3x1)-O reconstruction. Lower λ_s corresponds to lower T_c and overall poorer superconducting performance. Therefore, our studies strongly corroborate a strong body of previous literature that has hypothesized that the oxide diminishes superconducting performance for both bare Nb and new materials built atop it. From this fundamental starting point, we can further demonstrate the effect that doping, alloying, and thin-film material growth on the Nb surface have on its superconducting performance.

5:30pm **AS-TuA-14 The Type of Ru Oxide on Ru(0001) Determines the Activity for the Decomposition of Silane**, *Ester Perez Penco*, *R. Bliem*, ARCNL

Hydrogen plasma is commonly applied for the cleaning of functional surfaces, because it effectively removes most surface oxides and carbon-based deposits by reacting to form volatile species. However, this etching

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by hydrogen plasma also occurs for other elements, such as Si, which is widely abundant and forms silane gas (SiH_4) when exposed to hydrogen radicals and ions. The resulting silane molecules can serve as a means to transport Si through the plasma setup and lead to Si redeposition. Typically, Si growth from silane only occurs at specific conditions, often involving high surface temperatures. However, in the presence of catalytically active materials such as Ru and Ru oxide, decomposition of silane occurs already at significantly milder conditions. The interaction mechanisms of silane with the surfaces of Ru and its oxides and the criteria for the deposition of Si, however, are unclear.

Here, we present an in situ study of the mechanism that leads to plasma-assisted deposition of Si on Ru surfaces. We isolate the interaction of the transport agent, silane gas, with Ru(0001) single-crystal surfaces using near-ambient pressure X-ray photoelectron spectroscopy (XPS). A comparison of Ru metal to a thin, defective type of Ru oxide and bulk-like RuO_2 demonstrates a decisive impact of surface oxidation on the reaction with SiH_4 and the nature of the deposited Si. On Ru metal, silane decomposition is barrierless and results in the formation of Ru silicide. The initial layers of a (metastable) Ru oxide structure readily catalyze the deposition of Si, forming a Ru-Si-O compound that consumes the Ru oxide phase. Already a few nanometers of the bulk-like RuO_2 phase, on the other hand, are observed to be fully inert towards the decomposition of silane at room temperature. This striking difference between two similar oxides is attributed to their different density surface vacancies, which aid the dissociation of SiH_4 .

Our in situ XPS results demonstrate that the type of Ru oxide and its structural integrity is decisive for surface chemistry of Ru under oxidizing conditions. The contrast of facile silane decomposition for a thin defective oxide and its full inhibition for bulk-like RuO_2 serves as an illustration of the influence of seemingly subtle changes to the surfaces of materials with a wide application potential.

Applied Surface Science

Room 117 - Session AS-WeM

Quantitative Surface Analysis

Moderators: David Morgan, Cardiff University, UK, **Samantha Rosenberg**, Lockheed Martin

8:00am **AS-WeM-1 Analyzing the Extrinsic Inelastic Background of HAXPES Spectra Accounting for X-Ray Extinction in an Iron Oxide Finite Thickness Film**, *Dulce-Maria Guzman-Bucio*, O. Cortazar-Martinez, CINVESTAV-Unidad Queretaro, Mexico; *D. Cabrera-German*, Universidad de Sonora, Mexico; *J. Torres-Ochoa*, Universidad Politecnica de Juventino Rosas, Mexico; *A. Carmona-Carmona*, CINVESTAV-Unidad Queretaro, Mexico; *O. Ceballos-Sanchez*, Universidad de Guadalajara, Mexico; *W. Limestall*, *Z. Lee*, *J. Terry*, *M. Warren*, Illinois Institute of Technology; *A. Herrera-Gomez*, CINVESTAV-Unidad Queretaro, Mexico

The extrinsic inelastic part of the background is part of all photoemission spectra. Its identification and modeling, as well as other background contributions, play a crucial role in assessing the peak signal used in the quantification of chemical composition. However, existing methods cannot directly apply to finite-thickness films because they only apply to semi-infinite-homogeneous samples [1]. Moreover, they are not appropriate for spectra obtained with Hard X-ray Photoemission Spectroscopy (HAXPES), where the mean free path of the photoelectrons may be comparable to the absorption length of the photons at certain incident angles. In this study, we model the extrinsic inelastic background for photoemission spectra for a finite-thickness Fe₂O₃ film for which a grazing X-ray incident angle was employed. We analyzed Fe 2s, 2p, 3s, and 3p photoemission spectra acquired with synchrotron light at eight photon energies around the Fe 1s threshold at Beamline 10-ID-B at the Argonne National Laboratory. Our calculations assume a straight-line inelastic scattering path and account for the decay of the X-rays as they travel through the sample [2]. It was assumed that the inelastic electron cross section (λK) for iron oxide does not change drastically for electron primary energies higher than 2 keV, and one acquired at this primary electron energy was employed [3]. The comparison with the experimental data and information about sample processing shows great agreement.

This presentation summarizes the requirements and challenges involved in correctly analyzing the extrinsic inelastic background of HAXPES data. This includes using appropriate inelastic mean-free paths and effective attenuation lengths. Obtaining REELS data along with photoemission data, and calculating inelastic electron cross sections for primary excitation energies in the hard X-ray regime is essential.

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

[2] A. Herrera-Gomez, The photoemission background signal due to inelastic scattering in conformal thin layers -Internal Report, 2019.

[3] N. Pauly, F. Yubero, J.P. Espinós, S. Tougaard, Optical properties and electronic transitions of zinc oxide, ferric oxide, cerium oxide, and samarium oxide in the ultraviolet and extreme ultraviolet, Appl. Opt. 56 (2017) 6611–6621. <https://doi.org/10.1364/AO.56.006611>.

8:15am **AS-WeM-2 Non-Destructive Characterization of Multi-Layered Thin Films Using XPS, HAXPES and Structure Modeling in StrataPHI**, *N. Biderman*, *D. Watson*, *Kateryna Artyushkova*, 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 the composition of depth profiles and layer thicknesses, traditionally with Al K α (1486.6 eV) X-ray beams for depths up to 5–10 nm below the surface. In recent years, new ARXPS capabilities have been added to Physical Electronics XPS scanning microprobe instruments including Cr K α (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 K α and Cr K α 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. Such added StrataPHI capabilities allow for scientists and engineers in metrology and research & development to analyze multi-layered thin films and ultrathin 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.

8:30am **AS-WeM-3 The Challenge of Quantifying Photoemission Spectra Using Multiple Photon Energies**, *Thierry Conard*, *A. Vanleenhove*, IMEC, Belgium; *I. Hoflijk*, *I. Vaesen*, IMEC Belgium **INVITED**

The development of Photoemission spectroscopy in laboratories during the last decades has been focused on the use of AlK α radiation. Extensive work has been performed to tackle the issue of quantification of acquired spectra. These include aspects such as the determination of sensitivity factor, understanding spectral background, determining transmission function of spectrometers, and understanding electron transport inside materials (inelastic mean free path, ...).

The use of higher energy photons (HAXPES) has the potential to significantly increase the application field of PES due to its larger depth information making it more suitable for multilayers systems. One of the major limitations of HAXPES is the strong decrease of the photoemission cross-section at higher photon energy which, until a few years ago limited the use of HAXPES to synchrotron, where higher photon flux are achieved than in laboratory instruments. As such, the challenges to quantify HAXPES spectra do not differ significantly from lower photon energy experiment, but this was not the prime focus of synchrotron-based experiment. With the introduction of performant laboratory-HAXPES systems a few years ago, the need of better quantification for HAXPES has strongly been increasing.

In this presentation, we will start by presenting examples of the efforts made regarding the development of reliable quantification protocols, based, as for AlK α -based PES data, on the determination/analysis of sensitivity factors, background, transmission function, ...

Next to the “classical” challenges, some additional aspects need (more often) to be considered. First, energy referencing is critical for chemical state quantification. It is however more complex than with lower energy PES as it is very impractical to use contamination peak for referencing and the likelihood of vertical potential variations increases. Second, thanks to the larger photon energy, for many elements, additional photoemission peaks are available for analysis and peak-independent quantification would be interesting. For both aspects, we will present examples of applications and improvement.

Unfortunately, even if all the above-mentioned challenges would be solved, depending on the scientific question to be answered a single experiment may require the use of multiple photon energies, for instance for varying the analysed depth or improving on the chemical identification. We will discuss strategies to combine analysis with multiple photon energies to achieve the best possible understanding of the studied system. This will include consideration about results presentation for a better understanding by non-specialist.

9:00am **AS-WeM-5 Incorporating HAXPES Into Routine Industrial Surface Chemical Analysis**, *Christopher Young*, HP ADL; *D. Zheng*, HP ADL, Singapore; *M. Brumbach*, *W. Stickle*, HP ADL

The application of photoelectron spectroscopy in an industrial setting has generally employed Al K α and Mg K α radiation. Both of these sources have relatively narrow natural linewidths and are straightforward to handle. As all elements have an observable transition in a reasonable energy window when acquiring survey data with these energies, identifying the peaks and measuring high-resolution spectra for chemical state information has become fairly straightforward. Handbooks and spectral databases are readily available to aid an analyst. In addition to the Al and Mg sources, analysts may employ other materials such as Ag or Zr, as well as routinely using monochromatic Al K α x-rays. In many cases a reason for switching between x-ray sources is to ‘move’ Auger lines away from a photoelectron peak of interest, or even to resolve a specific Auger transition.

The use of hard x-ray sources in the laboratory has opened up new and exciting approaches to analyses. We will present some of our recent work regarding the creation of a HAXPES handbook for many common industrial materials (much of which will be published in Surface Science Spectra), including our protocols and acquisition methods and the limitations therein. We will also discuss the investigation of surface composition from the perspective of photoionization cross sections and illustrate how HAXPES provides a way for an analyst to readily quantify trace amounts of a material in a matrix where interference from spectral features or low

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sensitivity would otherwise prevent it. Finally, we will discuss some applications in our laboratory of the greater depth of analysis offered by Cr K α sources.

9:15am **AS-WeM-6 Beyond the Surface: A Simple Algorithm for Obtaining Surface-Free Depth Distribution Information from Combined XPS and HAXPES Spectra**, *Benjamen Reed*, National Physical Laboratory, UK; *J. Counsell*, Kratos Analytical Limited, UK; *A. Shard*, National Physical Laboratory, UK

There is a recurrent demand from the semiconductor, energy, and coatings industries to measure the chemical state of elements in subsurface layers. X-ray photoelectron spectroscopy (XPS) has unparalleled capabilities for chemical state measurements, but it has a limited information depth, typically around 10 nm for instruments using an Al K α X-ray source. The traditional method for measuring subsurface chemistry is to perform a depth profile, alternating ion beam sputtering to remove surface layers and XPS measurements. Gas cluster ion beam technology has enabled damage-free sputtering of organic materials, but low sputtering rates for inorganic materials gives impractical experiment durations. Increasing the energy per atom in clusters will typically improve sputtering rates but also generates a thin altered, or damaged, layer either through chemical changes or preferential removal of elements. Some materials are particularly sensitive to ion sputtering, and so will exhibit sputtering damage regardless of parameters used during depth profiling.

To aid in the analysis of these sputter sensitive materials, we present a data processing algorithm which attempts to isolate the spectroscopic information of the undamaged subsurface material from the damaged surface material during a depth profile. The algorithm utilises the different intensity depth distributions that arise from Al K α and Ag La X-ray generated spectra. An empirically determined scaling parameter is used to equate the surface intensity contribution from Al K α and Ag La X-ray generated spectra, allowing a difference spectrum to be obtained that has a surface-free depth distribution, and therefore reduces (or completely removes) the intensity contribution from the sputter damaged layer. This method also works for very thin overlayers on homogenous materials, such as native oxides or adventitious carbon contamination.

9:30am **AS-WeM-7 Depth Differentiated Surface Analysis by a Combination of XPS, HAXPES and Ion Scattering Spectroscopy**, *Paul Mack*, Thermo Fisher Scientific, UK

Complementary multi-technique surface analysis has been available on XPS systems for many years. It is only recently, however, with the advent of more user-friendly software interfaces that these complex experiments have become routinely accessible by all users. XPS systems with easily switchable monochromated X-ray sources are now commonplace, allowing the analyst to switch between Al-K α X-rays and some other higher energy photon source (Ag-La, for example). The use of two different X-ray energies enables some level of effective depth profiling without having to physically sputter the sample with an ion source.

XPS is known as a surface sensitive analytical technique, with Al-K α X-rays typically enabling analysis from the top 10-15nm of the surface, depending on the material. With a Ag-La monochromated source, the sampling depth may be similar for the photoelectron signals in the higher binding energy portion of the spectrum but up to double the sampling depth for the higher kinetic energy XPS peaks. If the analyst wants to probe the very top surface, including the top monolayer, then a different analytical technique is required. Ion Scattering Spectroscopy (ISS) is even more surface sensitive than XPS and when combined with XPS and its higher energy counterpart, HAXPES, a far more comprehensive picture of the surface composition and profile can be developed.

In this work, XPS, HAXPES and ISS have been combined on a XPS system enabling non-destructive depth differentiated analysis of a variety of samples. By bringing all three techniques together the depth distributions of elements and chemical states, from the top monolayer to beyond 20nm into the surface can be investigated.

9:45am **AS-WeM-8 Angle-Resolved XPS Depth Profiling for Extreme Ultraviolet (EUV) Lithography Optics Research – Monoatomic vs Cluster Ion Source**, *Veronique de Rooij-Lohmann*, *S. Mukherjee*, TNO Science and Industry, the Netherlands; *J. Counsell*, Kratos Analytical Limited, UK

In the Semicon Equipment Life-time department of TNO, X-ray photoelectron spectroscopy (XPS) analysis is utilized for characterization of optical surfaces, particularly mirrors and reticles for extreme ultraviolet (EUV) lithography. This study focuses on assessing the sensitivity of XPS depth profiling to multilayer mirrors which are similar to the EUV mirrors.

A commercial Ru-capped Mo/Si multilayer mirror was annealed in vacuum at 330 °C for 48 hours, to induce thermal degradation, i.e. intermixing and oxidation. Pre and post-annealing, traditional XPS depth profiling was conducted using a monoatomic Ar ion-gun.

However, monoatomic Ar⁺ depth profiling results in artefacts because preferential sputtering of light elements alters the stoichiometry, while ion-induced intermixing compromises layer contrast. Development of sputtering methods that reduce those artefacts is therefore of importance.

To address these challenges, we explore the potential of a Gas Cluster Ion Source (GCIS), known for minimizing the said artefacts. While GCIS is gaining traction in XPS, its applicability to EUV mirror analysis requires validation because the ion-solid interaction is material-dependent.

Moreover, given the limited thickness of the layers in an EUV-mirror compared to the XPS information depth, we also investigated the combination of sputter depth profiling with angle-resolved (AR-)XPS to enhance the surface sensitivity. The results are shown in Figure (a) and (b). This comparative study between traditional XPS depth profiling and GCIS, along with the exploration of AR-XPS, provides insights into optimizing analysis techniques for EUV mirrors and reticles. These findings inform further development towards metrology and understanding of EUV optics degradation.

11:00am **AS-WeM-13 Femtosecond Laser Ablation (fs-LA) – A New Approach to XPS Depth Profiling**, *Simon Bacon*, Thermo Fisher Scientific, UK; *S. Sweeney*, University of Glasgow, UK; *S. Hinder*, University of Surrey, UK; *A. Bushell*, *T. Nunney*, *R. White*, Thermo Fisher Scientific, UK; *M. Baker*, University of Surrey, UK

XPS depth profiling is a widely employed analytical technique to determine the chemical composition of thin films, coatings and multi-layered structures, due to its ease of quantification, good sensitivity and chemical state information. Since the introduction of XPS as a surface analytical technique more than 50 years ago, depth profiles have been performed using ion beam sputtering. However, many organic and inorganic materials suffer from ion beam damage, resulting in incorrect chemical compositions to be recorded during the depth profile. This problem has been resolved for most polymers by using argon gas cluster ion beams (GCIBs), but the use of GCIBs does not solve the issue for inorganics. A prototype XPS depth profiling instrument has been constructed that employs a femtosecond laser rather than an ion beam for XPS depth profiling purposes. This novel technique has shown the capability of eradicating chemical damage during XPS depth profiling for all initial inorganic, compound semiconductor and organic materials examined. The technique is also capable of profiling to much greater depths (several 10s microns) and is much faster than traditional ion beam sputter depth profiling. fs-LA XPS depth profile results will be shown for selected thin films, coatings, multilayers and oxidised surfaces and the outlook for this new technique discussed.

11:15am **AS-WeM-14 Top Atomic Layer Analysis of Bimetallic Nanoparticles by Low-Energy Ion Scattering (LEIS)**, *P. Brüner*, IONTOF GmbH, Germany; *D. Niedbalka*, *P. Abdala*, *C. Müller*, ETH Zürich, Laboratory of Energy Science and Engineering, Switzerland; *Thomas Grehl*, IONTOF GmbH, Germany

The composition of the outer atomic layer often differs significantly from subsequent layers. Since the performance of a heterogeneous catalyst heavily depends on its outer atomic layer, high surface sensitivity analytical techniques are required. Most available surface analytical techniques probe to a depth of at least a few nm. Any result will thus be an average over the first few (or many) monolayers, such that unique properties of the outer monolayer may be missed due to the diluted effect on the analysis result.

Low energy ion scattering (LEIS) is the only technique available that selectively probes the elemental composition of the outer atomic layer [1]. This is achieved by bombarding the sample surface with noble gas ions at an energy of some keV. These primary ions may scatter from surface atoms, and their characteristic energy loss is a measure for the mass of the scattering partners. Evaluating the energy spectra of the backscattered primary ions results in the quantitative elemental composition of the outer monolayer, since neutralization effectively suppresses the signal from scattering events below the outer surface.

Since LEIS is not sensitive to surface charging and topography, it is routinely applied to study (even supported and dispersed) nanoparticles and their terminating atomic layer. This contribution will introduce this application including results from several sample systems. The core results are from monometallic Co and Pt as well as bimetallic CoPt nanoparticles with varying Co/Pt ratios prepared on an SiO₂ support with a total metal loading

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of 1.5 – 4 wt. %. The catalysts were activated in a 10 % H₂/N₂ mixture at 800 °C for 1 h, resulting in average particle sizes ranging from 1.7 – 3 nm.

LEIS analyses were conducted using a Qtac 100 (IONTOF GmbH) with a double toroidal electrostatic analyzer optimized for high sensitivity and mass resolution, allowing for top atomic layer analysis without significant surface damage by the probing ion beam.

3 keV He⁺ ions were used for overview scans, as all elements C and heavier can be detected by He⁺ analysis. Subsequent analysis with 5 keV Ne⁺ ions offers improved mass resolution and sensitivity for heavy elements. For some of these samples, sample pretreatment is more challenging than usual, due to the H physisorption on Pt which must be reproducibly reduced to yield robust results.

The LEIS results relate the bulk composition of the CoPt nanoparticles to their surface composition, catalytic activity and stability. Reference samples were used to determine the precise surface coverage of Co and Pt.

[1] Cushman, C. V. et al., *Analytical Methods* **2016**, 8, 3419

11:30am **AS-WeM-15 Multilayer Adhesives-Ideal Samples for Showcasing GCIB Profiling Capabilities**, *Michaeleen Pacholski, B. Caruso*, Dow Chemical Company; *I. Uhl*, Dow Chemical Company, France; *A. Peera*, dow; *D. Keely, E. Glor*, Dow Chemical Company

There are many manufacturing methods that can produce multilayer coatings, but for pressure sensitive adhesives there has been growing use of curtain coaters that can create a multilayer coating in a single step. This allows manufacturers to balance the performance and cost of each layer of the coating to the application. Most of these adhesives are around 25 μm thick, meaning accessing buried layers, which cannot be delaminated, has involved laborious sample preparation prior to the application of GCIB profiling. With the application of this multilayer coating technology new questions are being asked of the analytical group that include: Do the adhesive layers mix? Do surfactants and tackifiers migrate between the layers? If the adhesive fails cohesively, in which layer does it fail? In this presentation the curtain coating method and measurements of importance in the liquid state will be discussed, as well as GCIB approaches to answer the questions above.

11:45am **AS-WeM-16 Similarities between Silicon and Aluminum with Suboxides Formation Using XPS Spectra**, *Orlando Cortazar-Martinez, D. Guzman Bucio, J. Torres Ochoa, C. Gómez Muñoz, J. Raboño Borbolla, A. Herrera-Gomez*, CINVESTAV-Unidad Queretaro, Mexico

Aluminum, recognized as a reactive metal, rapidly reacts with oxygen to form a dense protective layer of aluminum oxide. Its valence band contains three electrons, which can be shared to form Al¹⁺, and Al²⁺, and Al³⁺ oxidation states; the stable form is the latter, there have been reports of the presence of the first two.

Initial oxidation stages of aluminum were achieved by exposing the surface to a precisely controlled ultra-pure oxygen atmosphere with varying gas dosages. The metallic and oxidized film was characterized with angle-resolved X-ray photoelectron spectroscopy; the data was analyzed with state-of-the-art techniques. Two surprising results were found: 1) the appearance of two extra peaks in the Al 2p spectra, corresponding to Al¹⁺, and Al²⁺ at the interface; and 2) a protrusion-mode growth of Al₂O₃. The first shows many similarities with silicon, which is the next element in the periodic table. The second is also surprising because, contrary to current perception, the oxide does not grow conformally in the initial oxidation stages; this contrasts with silicon because it does grow conformally from the very initial oxidation.

This work was partially financed by Proyecto Fronteras 58518, Conahcyt, Mexico.

[1] A. Herrera-Gomez, F. Servando Aguirre-Tostado, and P. Pianetta, Formation of Si¹⁺ in the early stages of the oxidation of the Si[001] 2 × 1 surface, *Journal of Vacuum Science & Technology A* 34, 020601 (2016).

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

12:00pm **AS-WeM-17 3kV Vertical Gallium Nitride Photoconductive Semiconductor Switches**, *Geoffrey Foster, A. Koehler, A. Jacobs, K. Hobart*, Naval Research Laboratory; *S. Lowery, S. Atwinmah, S. Mahmud, R. Khanna*, University of Toledo; *J. Leach*, Kyma Technologies; *M. Mastro*, Naval Research Laboratory

We made a 3 kV vertical GaN photoconductive semiconductor switch that has 7 orders of magnitude on/off current. Vertical PCSSs carry the potential to outperform conventional unipolar semiconductor power devices. PCSSs become conductive after the absorption of light. Wide bandgap PCSSs, are desirable due to high critical electric field strength, high electron saturation velocity, and to provide high power ultrafast devices. Lateral GaN PCSSs have been demonstrated with a fast turn on time and a high amount of on-current. Vertical GaN PCSS have been shown to operate with below bandgap excitations. A device operating with band gap excitation would be preferred for high-powered switching, as it allows faster response time and faster switching speeds. Conventional unipolar power semiconductor devices are limited by the thickness of the drift layer, needed for voltage hold-off, but adds resistance to the conduction path. A PCSS can have a semi-insulating layer in lieu of a drift layer. The conductivity of the semi-insulating layer can be optically modulated, allowing for free-carrier injection. Fast switching speeds can be obtained by optical modulation, which optically isolates the sensitive gate driver control circuitry from the high-power switch and associated electronic noise.

One hundred micrometers of GaN was grown on an N+ GaN substrate by HVPE, with a carbon doping concentration of 1x10¹⁸ cm⁻³ to produce vertical PCSS diodes. Electrodes of Ti/Al/Ni/Au were formed into a 615 μm diameter circular patterns by lift-off on the top surface. Within the circles, a constant area of optically exposed GaN was left without metal. Square areas with sizes varying in size from 20 to 200 microns per side. Different devices were used to investigate the effects of collection area size outside of the metal contact area. Blanket Ti/Au was deposited on the backside of the wafer. I-V measurements were then performed by using a 3W, 365 nm, 46.24 mm² COTS LED. Electrical measurements were acquired at an optical power density of 0.102 W/cm². Two different resistance values were found, 1.37 Ω-cm² if the device was optically exposed and 1.42 Ω-cm² if the device was not. An additional 100 μm perimeter of a collection area outside the device accounts for the resistance variation. Devices exhibited a maximum current density of 3.63 A/cm² at 5 V. In the off state, devices were measured to have a current of 459 nA/cm² at 3 kV. Photoionization spectroscopy under monochromatic light shows a photoresponse excitation at the band gap and a carbon related excitation at 3.1 eV incident photon energy, with an on/off current of 7 and 3 orders of magnitude respectively under 5V forward bias.

Applied Surface Science Room 117 - Session AS-WeA

Advanced Materials and Methods

Moderators: Tanguy Terlier, Rice University, Julia Zakel, IONTOF GmbH, Germany

2:15pm AS-WeA-1 Ion Migration and Chemical Phenomena in Functional Materials: Correlative Studies via Combined AFM/ToF-SIMS Approach, Anton Ievlev, Oak Ridge National Laboratory **INVITED**

The performance of various electronic devices is defined by the delicate interplay of electrical response and charge carrier migration at the nanoscale. Although physical behavior and macroscopic functional response of these materials is well established, intrinsic chemical phenomena associated with ionic motion or localized electrochemical reactions can dramatically alter their behavior and thus restrict area of utilization. Over the last decade, advancements in development of novel nanoscale characterization tools such as atomic force microscopy (AFM) have revolutionized our understanding of the electrical and mechanical response of materials; however, *dynamic* electrochemical behavior and ion migration remain poorly understood. Recently time-of-flight secondary ion mass spectrometry (ToF-SIMS) has proven to be effective tool for characterization of static chemical states in energy materials. However, its application to study of dynamic electrochemical processes still requires development.

Here we introduce approach based on combined AFM/ToF-SIMS approach for correlated studies of the dynamic chemical phenomena on the nanoscale in operando conditions. Being used for characterization of the range of electronic materials, including ferroelectrics, photovoltaics and memristors it allowed direct observation of the ionic migration within the device in externally applied electric fields, which is important for fundamental understanding of the material functionality. Altogether, developed approaches enable direct characterization of interplay between chemical and functional response in variety of materials, which aids in the development and optimization of novel devices and applications.

This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility and using instrumentation within ORNL's Materials Characterization Core provided by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy.

2:45pm AS-WeA-3 Elemental and Chemical Quantification of Porous Transport Electrodes with X-Ray Photoelectron Spectroscopy Analysis and Scanning Electron Microscopy – Energy Dispersive X-Ray Spectroscopy, Lonneke van Eijk, Colorado School of Mines; J. Foster, Colorado School of Mines, USA; S. Khandavalli, National Renewable Energy Laboratory; L. Ding, University of Tennessee, Knoxville; G. Stelmachovich, Colorado School of Mines, USA; S. Mauger, National Renewable Energy Laboratory; F. Zhang, University of Tennessee, Knoxville; A. Paxson, Plug Power; S. Pylypenko, Colorado School of Mines, USA

Optimization of proton exchange membrane water electrolyzers (PEMWEs) is essential to ensure reliable hydrogen generation and societal transition towards greater hydrogen energy use. Further improvements are crucial for facilitating the widespread adoption of hydrogen as a sustainable energy source. Various avenues are under exploration to advance PEMWEs further, aiming for increased activity and stability of catalysts, alongside the optimization of catalyst layer (CL) structure. This work focuses on the development of porous transport electrodes (PTEs), consisting of an iridium oxide-based catalyst layer and a titanium-based porous transport layer coated with a platinum protective layer. This project explored several CL deposition methods, including airbrush, rod coating, ultrasonic spray coating, and electrodeposition, to achieve homogeneous CL coatings and control of catalyst loadings. Additionally, post-treatments of PTEs were explored to elucidate the interplay between activity and stability of CLs and further optimize the performance.

The main goal of this study was the development of quantitative metrics that can be used for comparative studies of the quality of CL coatings and their performance. The first part of my talk will discuss scanning electron microscopy – energy dispersive X-ray spectroscopy (SEM-EDS) analysis of a series of PTEs produced with various routes. SEM-EDS was used to assess the elemental composition and the distribution of elements of interest. In addition to qualitative assessment of SEM-EDS images, this study also implemented quantitative metrics based on Pt:Ir ratios. The

implementation of proper characterization of these PTEs can help aid future decisions on which fabrication and processing parameters should be used to achieve coatings with desired quality and loadings. This approach can also be used for quality control, enabling quick screening of commercially produced samples. The second part of my talk will discuss the X-ray Photoelectron Spectroscopy (XPS) data analysis for chemical analysis of PTEs annealed under various environmental conditions and temperatures, with the goal of elucidating the impact of these parameters on material properties and electrochemical performance. This talk will discuss results and challenges associated with the analysis of Ir-based materials and will highlight trends between several quantitative metrics derived from XPS data and their correlations with electrochemical parameters. The findings not only contribute to advancements in PEMWE technology but also underscore the importance of the identification of simple metrics that can be used for trend identification in complex datasets.

3:00pm AS-WeA-4 Comprehensive Characterization of Porous Transport Layers and Porous Transport Electrodes with Time-of-Flight Secondary Ion Mass Spectrometry, Genevieve Stelmachovich, L. van Eijk, J. Foster, Colorado School of Mines; L. Ding, University of Tennessee, Knoxville; S. Ware, J. Young, National Renewable Energy Laboratory; F. Zhang, University of Tennessee, Knoxville; A. Paxson, Plug Power Inc.; G. Bender, National Renewable Energy Laboratory; D. Cullen, Oak Ridge National Laboratory; S. Pylypenko, Colorado School of Mines

Proton Exchange Membrane Water Electrolysis (PEMWE) is a promising technology towards the realization of the hydrogen economy. PEMWE components include the porous transport layer (PTL), a sintered or felt titanium material, and the adjacent catalyst layer (CL) which is typically made with IrO_x or IrRuO_x catalyst. Recent advancements in manufacturing have pushed towards the fabrication of porous transport electrodes (PTEs), where the anode CL is directly coated onto the PTL. To mitigate degradation of the PTL and improve the interface between CL and PTL, PTLs are typically coated with a thin protective coating, usually Pt. This leads to a complex layered PTE structure that consists of catalyst layer, protective coating, and porous transport layer (IrO_x/Pt/Ti or IrRuO_x/Pt/Ti) and is difficult to characterize.

Previously, we have demonstrated Time of Flight Secondary Ion Mass Spectrometry (TOF SIMS) as a powerful characterization technique for the qualitative and comparative characterization of PTLs, enabling the assessment of the interface between protective coating and PTL. Further, we focused on analysis of protective coatings with a focus on their thickness. We correlated TOF SIMS data and Scanning Transmission Electron Microscopy (STEM) measurements to demonstrate that TOF SIMS can be used to reliably compare coatings with different thicknesses despite the complex morphology of the substrate. More recently we used TOF SIMS to characterize a series of PTEs made with electroplated IrRuO_x catalyst that underwent various post-treatments. A combination of spectroscopy, imaging, and depth profiling analysis was utilized to identify chemical and spatial differences. This data was combined with Scanning Electron Microscopy Energy Dispersive X-Ray Spectroscopy (SEM-EDS), STEM, and X-Ray Photoelectron Spectroscopy (XPS) analysis to highlight the complementary nature of TOF SIMS analysis and demonstrate the need for comprehensive characterization with multiple techniques.

3:15pm AS-WeA-5 Characterization of the Nanostructure and Composition of Mollusc Shells Using Advanced Spectroscopic and Imaging Techniques, David Morgan, Cardiff University, UK

Biomineralization is an important field, informing researchers across many disciplines, on materials design, understanding of evolution and the development of tissue-engineering. Molluscs biomineralize to form shells as a means of protecting their internal soft tissues and these strong shells have led to molluscs becoming the second largest invertebrate phylum with over 70,000 species.

These shells are organo-mineral composite structures consisting of two key components - an inorganic carbonate mineral and organic macromolecules (e.g. proteins, polysaccharides). This complex structure imbues them with enhanced mechanical properties, such as high strength and fracture toughness. In recent years, much attention has been focused on the nacreous shell structure to replicate materials with similar strengths and toughness. To date, most research papers have focused on the microstructures of these shells, little work has been done on their nanostructure which represents a key gap in our knowledge of biomineralization since amorphous calcium carbonate nanostructures form the first building blocks of these hierarchical structures.

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The presented work focuses on the intricate nanostructure and composition of the Fluted Giant Calm (*Tridacna squamosa*) by means of Photo-induced Force Microscopy (PiFM) and X-ray Photoelectron Spectroscopy (XPS). We show that XPS unequivocally confirms the presence of calcium (Ca) and magnesium (Mg) within the z-axis of the shell matrix, whilst, PiFM unveils a multifaceted composition, indicating that the shell comprises a mixed-phase carbonate structure, intricately woven from both structured and amorphous aragonite and magnesite. Notably, PiFM analysis reveals a structural distinction between the Inner and Outer Shell layers, with the outer layers displaying distinct "zebra stripe" patterns, denoting magnesite and dolomite-like bonding that traverses the aragonite structure. This study significantly contributes to advancing our comprehension of mollusc shell structure and composition.

3:30pm AS-WeA-6 Development of Best Practices for Cryo-XPS – Opening the Possibility to New Sample Analysis and Paving a Route to Standardization, K. Zahra, *Liam Soomary*, Kratos Analytical Limited, UK; C. Moffitt, D. Surman, Kratos Analytical Inc.; J. Counsell, Kratos Analytical Limited, UK

Conventional x-ray photoelectron spectroscopy (XPS) has typically limited samples to solids, powders, and thin films due to the ultra-high vacuum (UHV) requirements of analysis. This has constrained the utilization of XPS in various industries (e.g. biological/ medical and battery manufacturing), due to the preparation requirements to create vacuum compatible samples often resulting in analysis in non-native environments. Developments in near-ambient pressure (NAP-XPS) and frozen hydrated sample (cryo-XPS) analysis is beginning to bridge these gaps. NAP-XPS systems are widely available at synchrotron facilities, with commercial instruments also on the market. However, beamtime is highly competitive and commercial instruments are currently expensive.

Previous comparisons in the literature between the two methods have shown both give comparable data [1]. Still the ability to maintain UHV conditions using cryo-XPS minimises surface contamination and provides higher signal intensity, therefore enabling shorter acquisition times. Cryo-XPS is also an accessory added to conventional XPS making it a cost-effective option.

Rate of cooling is a major consideration in cryo-XPS. Slow rates of freezing result in fewer nucleation sites, thus larger crystals, which cause cellular damage. Flash-freezing is essential to produce vitreous (amorphous, glass-like) ice, preventing crystal formation. In biological and medical research this preserves cellular structures and maintains a near-native state. It also preserves compounds, avoids surface restructuring, and minimises surface degradation. After vitrification, sample temperatures need to remain below -137 °C to prevent devitrification [2]. Thus, sample transfer between the load-lock and analysis chamber must be fast and dependable.

In this talk we hope to provide industry relevant guidelines for sample preparation with a focus on reproducibility using cryo-XPS. We will also demonstrate how layered analysis is achieved when cryo-XPS is coupled with Gas Cluster Ion Source (GCIS) etching to delve deeper into the surface. Finally, we will comment on directions for future improvements in the technique.

[1] M. Kjaervik et al., Comparative Study of NAP-XPS and Cryo-XPS for the Investigation of Surface Chemistry of the Bacterial Cell-Envelope, *Front. Chem.*, (2021) 9:666161. DOI: 10.3389/fchem.2021.666161

[2] G. Weisenberger et al., Understanding the invisible hands of sample preparation for cryo-EM, *Nat. Methods*, (2021) 18:5. DOI: 10.1038/s41592-021-01130-6

4:15pm AS-WeA-9 ASSD Student Award Finalist Talk: 3D ToF-SIMS Imaging of Polyethylene Oxide-Lithium Nitrate Electrolytes in Lithium Ion Batteries, *Reyhane Shavandi*¹, University of Illinois Chicago

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is increasingly used to reveal three dimensional atomic and molecular distributions in the solid-electrolyte interface (SEI) of lithium ion batteries [1,2]. Solid electrolytes were previously sandwiched between lithium foil and copper electrodes, subjected to charge-discharge cycling until electrical failure, then lithium dendrites responsible for failure were detected by post-mortem ToF-SIMS analysis [3]. However, the requisite mechanical removal

of the lithium foil prior to ToF-SIMS analysis can inadvertently remove some of the SEI. An alternate strategy was pursued here in which the lithium foil was replaced with thin layers of lithium evaporated *in vacuo* [4], allowing ToF-SIMS to follow the reaction of metallic lithium with the electrolyte. A micrometer-thick solid electrolyte composed of polyethylene oxide (~600 kDa) and lithium nitrate was slot dye coated onto a copper substrate and compared by ToF-SIMS with the same samples on which 10 or 100 nm thick layers of lithium were evaporated. 30 keV Bi³⁺ primary ions from a liquid metal ion gun were used to collect positive ion spectra during simultaneous sputtering with a 10 keV argon gas cluster ion beam (IONTOF M6, Münster, Germany). The depth profiles for NO₂⁺ representing the lithium nitrate salt, C₂H₅O⁺ representing polyethylene oxide and Cu₃⁺ representing the copper electrode indicated that the addition of lithium increased the total fluence of argon cluster ions through the solid electrolyte. A limited number of negative ion spectra were recorded that showed NO₂⁻ and Cu₃⁻ following similar trends as in their positive ion counterpart spectra. However, high NO₂⁻ signals persisted after the Cu₃⁻ signals leveled off and changes were observed in copper cluster secondary ions with lithium addition. These effects are discussed in terms of cluster ion-induced mixing or substrate roughening, and the higher sputtering efficiency expected for the polyethylene oxide and lithium nitrate compared to the copper substrate.

1. T. Lombardo, M. Rohnke, et al., *J. Vac. Sci. Technol. A* **41** (2023) 053207. <https://doi.org/10.1116/6.0002850>

2. Q. Ai, J. Lou, et al., *ACS Energy Lett.* **8** (2023) 1107. <https://doi.org/10.1021/acseenergylett.2c02430>

3. M.J. Counihan, S. Tepavcevic, et al., *ACS Appl. Mater. Interf.* **15** (2023) 26047. <https://doi.org/10.1021/acsam.3c04262>

4. M. Counihan, S. Tepavcevic, et al., *ACS Appl. Mater. Interf.* **15** (2023) 26047. <https://doi.org/10.1021/acsam.3c04262>

4:30pm AS-WeA-10 Understanding the Impacts of Battery Electrode Manufacturing Processes through Surface Characterization Techniques, *Mikhail Trought*, T. Kravchuk, S. Peczonczyk, A. Straccia, M. Nichols, Ford Motor Company

The automotive industry has collectively adopted the shift towards manufacturing lithium (Li)-ion battery powered electric vehicles (EVs) to mitigate the environmental impacts of internal combustion engine vehicles, and to meet the evolving government regulations. Manufacturing of Li-ion batteries, and in particular their electrodes, is multifaceted and consists of multiple process steps that can affect the chemical and physical properties of the battery materials, which directly influences the battery's performance. In this study, we have characterized model solvent-based Li-ion battery electrodes: NMC-based cathodes with polyvinylidene fluoride (PVDF) binder and graphite-based anodes with carboxymethyl cellulose (CMC) and styrene butadiene rubber (SBR) binders. The effects of the drying and calendaring manufacturing processes on the chemical properties and morphology were studied. X-ray photoelectron spectroscopy (XPS) and time of flight secondary ion mass spectrometry (ToF-SIMS) were used to assess the chemical composition of these battery materials after drying. In parallel, atomic force microscopy (AFM) was used to assess the battery electrode's morphology after drying and after exposure to mechanical stimuli similar to that of the calendaring process. The quality of the battery electrode is highly dependent on manufacturing processes; characterization techniques need to be implemented to understand how these processes affect the electrode and how that ultimately affects the battery's performance.

4:45pm AS-WeA-11 Characterization of Sodium Ion Batteries - from Postmortem to Operando, *Marcus Rohnke*, T. Ortman, D. Schäfer, J. Janek, Justus Liebig University Giessen, Germany

INVITED

Lithium-ion batteries (LIBs) have been at the forefront of energy storage technology since the early 1990s due to their relatively high energy density (260 Whkg⁻¹), reasonable cost (\$153/kWh), and long lifespan.[1] However, the high demand, lack of raw material availability, poor ecological, political and working conditions in the mining countries require new battery concepts. Despite their lower energy density (~150 Whkg⁻¹) compared to LIBs, sodium ion batteries (SIBs) appear to be an interesting alternative, especially for non-portable applications where weight is secondary. SIBs could be used for stationary storage of excess energy from renewable sources such as wind or solar power. Moreover sodium is the 6th most abundant element on earth and is more evenly distributed throughout the globe than lithium.

Researchers around the world are working on concepts for SIBs with liquid and solid electrolytes, so-called solid-state sodium ion batteries.[2] In most

¹ ASSD Student Award Finalist

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cases, the interface properties between the materials used determine the battery kinetics and long-term cycling behavior. Here surface analytical methods such as time-of-flight secondary ion mass spectrometry (ToF-SIMS) or X-ray photoelectron spectroscopy (XPS) play a key role, in combination with 3D analysis and cross-section preparation.[3] They offer the opportunity to learn more about interfacial processes taking place. This knowledge is essential for continuously improving the performance of batteries.

Within this talk we will give insights in our ongoing work on SIBs with liquid as well as solid electrolytes. We will highlight how SIMS, XPS, SEM and TEM can be used in combination with classical electrochemical methods to learn more about electrode and decomposition reactions in SIBs. The first example focuses on the interfacial kinetics in solid state Na batteries with the solid electrolyte NASICON ($\text{Na}_{3-x}\text{Zr}_2\text{Si}_2.4\text{P}_{0.6}\text{O}_{12}$). In the second example classical hard carbon electrodes from electrochemical cells with liquid electrolytes are characterized in 3D with a special focus on the so called solid electrolyte interface (SEI). Here a decomposition layer is formed, which has a significant impact to the cellular kinetics.

Funding was received through POLIS Cluster of Excellence – Post Lithium Storage.

[1] R. Zhao, S. Zhang, J. Liu, J. Gu, *J. Power Sources* **2015**, 299, 557–577

[2] D. Schäfer, K. Hankins, M. Allion et. al., *Adv. Energy Mater.* **2024**, 2302830

[3] T. Lombardo, F. Walther, C. Kern et al., *J. Vac. Sci. Technol. A* **41** **2023** 053207

5:15pm **AS-WeA-13 Surface Analysis of Engineered Particles for Improved Battery Performance and Stability**, *Jennifer Mann*, S. Zaccarine, Physical Electronics; I. Oladeji, ULVAC Technologies, Inc.; K. Suu, Ulvac Technologies, Inc., Germany; K. Artyushkova, Physical Electronics

We require next-generation battery materials to achieve optimal energy density, rapid charging capabilities, and extended device longevity, all while maintaining affordability and reliability. Lithium metal batteries present a promising alternative to lithium-ion batteries; however, they encounter stability issues such as unstable solid-electrolyte interphase (SEI) growth and the formation of lithium dendrites. Similarly, cathode materials with high energy density, such as nickel manganese cobalt (NMC), demonstrate stable performance at high potentials but are vulnerable to dissolution within the electrolyte and unstable SEIs. Engineered particles (Ep) offer a solution by stabilizing electrode interactions, thus enhancing battery safety, SEI formation, and overall performance. Nonetheless, batteries are multi-layered, complex systems with numerous components and interfaces, posing challenges to characterization. A comprehensive understanding of the chemical composition, distribution, and morphology of Ep-treated anodes/cathodes is essential for fabricating uniform, well-dispersed electrodes with high capacity, thereby optimizing battery performance.

Advancements in X-ray photoelectron spectrometers have broadened their capabilities to effectively tackle these hurdles. X-ray photoelectron spectroscopy (XPS) emerges as an ideal method for scrutinizing the thin layers and interfaces of battery materials, due to its surface sensitivity (approximately 10nm) and ability to discern chemical states. Multi-technique XPS instruments offer an array of operational modes and analytical choices, facilitating comprehensive characterization of battery materials. This presentation showcases the utilization of a fully automated, multi-technique scanning XPS/HAXPES microprobe to address various challenges in battery material analysis. It incorporates an inert environment transfer vessel for air-free handling, a microprobe X-ray source with sub-5µm spatial resolution for precise area selection in small-area spectroscopic analysis and chemical mapping, and the utilization of hard X-ray and cluster ion gun sources for examining buried interfaces without compromising the underlying chemistry. The combination of these powerful capabilities allows for thorough analysis of battery materials at both macroscopic and microscopic levels, establishing a clear link between the chemistry and performance of electrodes treated with Engineered particles (Ep).

5:30pm **AS-WeA-14 X-ray Photoelectron Spectroscopy for Battery Research Applications**, *Tatyana Bendikova*, A. Maity, N. Yahalom, Y. Steinberg, H. Weissman, B. Rybtchinski, M. Leskes, Weizmann Institute of Science, Israel

X-ray Photoelectron Spectroscopy (XPS), as a surface sensitive technique with the sensitivity down to single atomic layer, provides unique

information about elemental composition and chemical and electronic states of elements in the material. It is not surprising that XPS is considered as one of the prominent tools in battery research, which enables determination of the electrodes/electrolyte composition during battery cycling, detection of the interfacial phases and follow their structural and compositional variations through depth profiling using ion sputtering. We show two examples where XPS was successfully used for the study of: 1) Sulfur-based composite carbon nanotube cathodes;¹ and 2) solid electrolyte interphase (SEI) on Na-Ion anodes.²

In spite of high reliability of the XPS technique and its assorted capabilities it should be taken into consideration that experimental conditions (high vacuum requirements) and X-ray radiation damage might alter the composition of the studied sample and can be mistakenly interpreted as non-existent battery reaction products. We present here systematic study of the LiTFSI, a widely used component of the nonaqueous battery electrolytes. We show how pumping conditions and/or prolonged X-ray exposure result in continuous deterioration of the LiTFSI. We also suggest partial solutions for deceleration of the decomposition processes during XPS measurements.

Literature:

1. N. Yahalom et. al, *ACS Appl. Energy Mater.* **2023**, 6, 4511–4519.
2. Y. Steinberg et. al, *manuscript in preparation.*

5:45pm **AS-WeA-15 AVS National Student Award Finalist Talk: Superconducting the Substrate Mediated Growth Pathways and High-Field Interacting Behavior of Nb₃Sn Films for Particle Accelerator Cavities**, *Sarah Willson*¹, University of Chicago; A. Harbick, Brigham Young University; R. Farber, University of Kansas; H. Lew-Kiedrowska, V. Do, University of Chicago; M. Transtrum, Brigham Young University; S. Sibener, University of Chicago

Niobium is the highest temperature elemental superconductor, making it the standard material for superconducting radiofrequency (SRF) cavities in next-generation linear accelerators. These facilities require cryogenic operating temperatures (< 4 K) to limit the formation of superconductivity-quenching hot spots in the near-surface region of the cavity. Widespread efforts are underway both to increase the accelerating fields and reduce the cryogenic burden by improving SRF surfaces. A promising solution is to coat the Nb SRF surface with a Nb₃Sn thin film *via* Sn vapor deposition. The higher critical temperature and critical field makes Nb₃Sn an ideal candidate for capping Nb surfaces. However, persistent Nb₃Sn material defects at the film surface, such as stoichiometric inhomogeneities and surface roughness, preferentially nucleate vortices under high fields that limit the accelerating performance of Nb₃Sn surfaces.

As part of a widespread interdisciplinary effort to optimize SRF accelerating capabilities, this work aims to develop a comprehensive growth model for pristine Nb₃Sn films. The complex interplay between the underlying Nb oxide morphology, Sn coverage, and Nb deposition temperature are examined by depositing Sn vapor on model Nb surfaces in an ultrahigh vacuum (UHV) environment with *in situ* surface characterization capabilities. Fundamental studies were scaled up to visualize how nanoscale features on the Nb oxide surface influence Sn and Nb₃Sn nucleation on unpolished polycrystalline Nb surfaces. These film growth studies collectively demonstrate that the Nb substrate defect sites are critical for stabilizing Sn adlayers.

Furthermore, the morphologies of stoichiometric defects on fully grown Nb₃Sn surfaces were investigated with computational support to simulate how the structures and sizes of Sn-poor and Sn-rich features influence the nucleation of vortices during SRF operation. Nb₃Sn films were prepared under varying conditions to demonstrate how the final cooldown steps of the vapor deposition process influence the stoichiometric homogeneity of the within the first 100 nanometers of the Nb₃Sn surface. Results indicate that the diameter and embedment of elemental Sn islands significantly alter the expected vortex nucleation field for a given global Sn composition. Understanding the effect of Nb₃Sn stoichiometric defect morphology on the high-field vortex nucleation is essential to systematically assess how different surface defects attenuate the achievable accelerating performance of Nb₃Sn coated cavities.

6:00pm **AS-WeA-16 Silicon Wafer Doping with Mineral Films Prepared via Tethering by Aggregation and Growth**, *Peter Thissen*, KIT, Germany

We investigate a new doping process of silicon wafers without making use of any highly toxic or corrosive chemical substances. Ultra-thin films of

¹ AVS National Student Award Finalist

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minerals, like hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), are prepared via tethering by aggregation and growth (T-BAG) and processed by rapid thermal annealing [1]. A variety of minerals can be used to effectively form metal silicates in contact with silicon oxide. This process is mainly thermodynamically driven and has already been well-studied using calcium silicate as an example [2]. One of the most thermodynamically stable calcium silicate phases is wollastonite (CaSiO_3). The main advantage of such formed phases is that they do not need to be etched with HF in the final step of the semiconductor processing; the direct use of mineral acids such as HCl or H_2S is sufficient to remove unwanted reaction byproducts. The doping method used, which uses the T-BAG technique for sample preparation, is not without inherent limitations. Although this method is widely used due to its simplicity and effectiveness, it is important to recognize its disadvantages, in particular the tendency towards an uneven distribution of the dopants across the semiconductor material. This phenomenon leads to an inhomogeneity across the sample, thus setting clear limits to the accuracy and reliability of the doping process. Consequently, although the T-BAG method is simple in sample preparation, its tendency towards non-uniform doping distribution highlights the need for careful consideration and possible refinement of future doping strategies. Using IR spectroscopy, we have already observed that the mineral decomposes at low temperatures (~ 500 K). The transport of 'P' through the native silicon oxide is driven by a phase transformation into a more stable thermal oxide [3]. At around 1000 K, diffusion of phosphorus into the region below the surface of the oxide-free silicon is observed. Finally, from our in-situ IR measurements in combination with electrical impedance spectroscopy, we conclude that phosphorus (a) is transported through the silicon oxide, (b) diffuses into the oxide-free silicon, and (c) finally changes the electrical activity of the silicon wafer.

[1] Vega, A.; Thissen, P.; Chabal, Y. J., Environment-Controlled Tethering by Aggregation and Growth of Phosphonic Acid Monolayers on Silicon Oxide. *Langmuir* 2012, 28, 8046-8051.

[2] Thissen, P., Exchange Reactions at Mineral Interfaces, *Langmuir* 2020 36 (35), 10293-10306.

[3] Longo, R. C.; Cho, K.; Hohmann, S.; Thissen, P., Mechanism of Phosphorus Transport through Silicon Oxide During Phosphonic Acid Monolayer Doping. *The Journal of Physical Chemistry C* 2018, 122, 10088-10095.

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Room 117 - Session AS-ThM

Machine Learning and Data Evaluation

Moderators: Steve Consiglio, Tokyo Electron, Jeffrey Terry, Illinois Institute of Technology

8:00am **AS-ThM-1 Redox XPS: Reliable and Automatic Peak Fitting of XPS Chemical States**, Peter Cumpson, Sanispectra Ltd, UK; D. Devadasan, Thermo Fisher Scientific, UK; R. Weatherup, Oxford University, UK; S. Gazzola, University of Bath, U.K.; T. Nunney, Thermo Fisher Scientific, UK

At the AVS symposium in 2023 we introduced *Redox XPS*, which removes ambiguities in fitting narrow scan XPS spectra by gas-phase oxidation (or reduction), typically with the assistance of ultraviolet light, within the XPS instrument. Since then we have automated the procedure, so that for a set of samples on a sample block one obtains a montage of spectra, each montage representing a progression of oxidation state. This takes more "wall-clock" time, but no more operator time, than a single spectrum.

Redox XPS is useful to remove some ambiguities, especially around any very small peaks from unexpected elements that are otherwise difficult to identify, but the principal advantage of Redox XPS is the ability to do *automatic* peak-fitting in a reliable and quantitative way. Instead of comparing with spectra obtained using other instruments (for example libraries of spectra acquired on instruments which may have different transmission functions, energy calibrations or energy resolution) one can reach a reliable quantification from *relative* measurements within a set of spectra acquired on one instrument on the same day.

To extract peak shape and intensity corresponding to the plural chemical states originally present in the sample we here apply;

1. A regularization method to avoid over-fitting, by including constraints arising from the physics and chemistry of XPS peak shapes,
2. Non-negativity constraints (valid for all real spectra, where counts and concentrations can never be negative), and
3. A feature of the inelastic background that we identify for the first time, and that has somehow escaped the notice of the community for the 30 years or more that XPS background subtraction has been common.

This algorithm is tested on Redox XPS data from 12 different elements acquired automatically. In most cases (and at the expense of more instrument time) this solves the problem of peak-fitting that otherwise can take up the valuable time and skills of XPS experts. Further, the ability to automatically fit complex peak-shapes means that Auger features that have often been ignored in the past (due to their prohibitively complex line shapes) will become very useful to analyse quantitatively by this procedure. Most of the data we show are from progressive oxidation using UV and ozone, but we have also demonstrated reduction in some cases.

8:15am **AS-ThM-2 Exploring the Benefits of Automated, Redox Reactions in XPS Analysis**, Robin Simpson, T. Nunney, P. Mack, Thermo Fisher Scientific, UK

This presentation investigates the benefits of automated, in-situ redox reactions for the purpose of producing well controlled oxide growth on the surface of various sample types. The driving force behind using such a procedure is in the potential for generating a sequence of spectra from a progressively chemically-modified surface to remove ambiguities that can lead to misinterpretation, thus aiding in faster understanding of the unmodified surface. Our study presents XPS results from coupled stepwise oxidation/reduction of surfaces, to aid in resolving such ambiguities across a wide array of materials. We use gas-phase oxidation agents to control the redox states of a specimen, leveraging the logarithmic growth of oxide thickness. This oxidation is implemented using vacuum ultraviolet light (VUV) and the generation of ozone and gas-phase hydroxide free radicals close to the surface of the specimens within the entry-lock of the Thermo Scientific Nexsa surface analysis instrument. This work focusses on the benefits of automating this process to ascertain the potential merits of including it into a standard operating procedure for XPS analysis.

8:30am **AS-ThM-3 Fourier Denoising of X-ray Photoelectron Spectroscopy Data**, Matthew Linford, A. Lizarbe, K. Wright, Brigham Young University; J. Terry, Illinois Institute of Technology; D. Aspnes, Brigham Young University

There has long been something of a prohibition on the smoothing/denoising of X-ray photoelectron spectroscopy (XPS) data. In this talk, we reconsider this possibility.

Fourier analysis is powerful for data analysis because it allows one to separate the information in a spectrum in a way that is not possible in direct space. This separation takes place because information in spectra, including XPS spectra, is usually in point-to-point correlations, which ends up in low index Fourier coefficients, while noise is in point-to-point variations, which ends up in high index Fourier coefficients. One of the pillars of Fourier theory is the convolution theorem. It states that convolution in one domain (direct or reciprocal) is equivalent to multiplication in the other.

In this talk, we begin by evaluating the effectiveness of common smooths like the boxcar and Savitzky-Golay smooths. In both cases, these smooths are flawed. They lack the ability to fully remove high frequency noise from data. We then discuss the use of the Gauss-Hermite (GH) filter for removing noise from Fourier transformed XPS spectra. This adjustable filter is unity, or near unity, for lower index Fourier coefficients, but drops off smoothly to zero for the higher index coefficients. We show the use of this filter for a relatively broad Ag 4s XPS peak, a narrow scan (Ag 3d) with sharp, spin-orbit components, and a metal peak that shows a significant step in the baseline. Various positions of the GH filter are considered in each case (this filter function is adjustable). We compare our results to 'true' spectra obtained by significant signal averaging. We make the case that appropriate Fourier filtering of XPS data may have a useful place in XPS data analysis. We also provide cautions for using this capability.

8:45am **AS-ThM-4 Fourier Denoising of X-ray Photoelectron Spectroscopy Data. Applications to the carbon Auger D parameter, HAXPES, and EasyEXAFS**, Alvaro Lizarbe, K. Wright, G. Murray, G. Lewis, Brigham Young University; M. Isaacs, Diamond Light Source, UK; D. Morgan, Cardiff University, UK; D. Aspnes, North Carolina State University; M. Linford, Brigham Young University

We recently argued for the use of Fourier denoising with the Gauss-Hermite filter as a tool for separating the signal and noise in XPS spectra. The Gauss-Hermite filter more effectively removes high frequency noise from spectra than more traditional Savitzky-Golay and boxcar smooths. This type of approach works because noise is contained in point-to-point variations, while signal is in point-to-point correlations. In this talk, we discuss practical ways of implementing this capability. For example, the carbon Auger signal needs to be smoothed before it is differentiated to derive the D-parameter. Otherwise, the numerical differentiation blows up the noise. Denoising with the Gauss-Hermite filter effectively denoises these spectra. Furthermore, differentiation of this signal is then easily performed by differentiating (and summing the derivatives) of the individual harmonics associated with the discrete Fourier transform. HAXPES represents an important direction in modern XPS. However, the cross sections for photoemission are often considerably lower with the higher energy X-rays used in HAXPES. Accordingly, there are advantages associated with the denoising of these spectra. Finally, EasyEXAFS is an important, laboratory-based way of performing EXAFS. However, again, in a number of cases, the signal-to-noise ratios of the signals are low. Again, the denoising of these signals is advantageous. In addition to demonstrating these new capabilities, we provide guidelines and cautions for using them.

9:00am **AS-ThM-5 ASSD Student Award Finalist Talk: Stitching, Stacking and Multilayering: Practical Evaluation of ToF-SIMS Data with Machine Learning**, Sarah Bamford¹, W. Gardner, D. Winkler, La Trobe University, Australia; B. Muir, CSIRO Materials Science and Engineering, Australia; P. Pigram, La Trobe University, Australia

INVITED

Time of flight secondary ion mass spectrometry (ToF-SIMS) is a powerful analytical technique capable of collecting mass spectral information in one, two and three spatial dimensions. ToF-SIMS images and depth profiles are large and complex hyperspectral data sets. Interpretation requires that the complexity of these data sets is reduced. For two-dimensional (2D) data, individual ion peaks are often extracted and overlaid or for three-dimensional (3D) data, a selection of characteristic peaks are plotted in one dimension as a function of depth. These well-established methods are ideal for known or simple samples. However, for complex or unknown samples, these methods struggle to convey the depth of information captured within

¹ ASSD Student Award Finalist

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the data set. Furthermore, the choice of displayed ion peaks has the potential to impart user bias and make a significant difference to the interpretation of results.

Unsupervised machine learning, specifically self-organizing maps with relational perspective mapping (SOM-RPM), allows considered analysis of complex unknown samples. The SOM-RPM approach creates a color-coded similarity map in which changes in color are specifically graded to accord with changes in molecular state, by examining the totality of the data set. By pairing ToF-SIMS and SOM-RPM, the complete hyperspectral data set in 2D or 3D can be intuitively visualized, providing a unique picture of the local and global mass spectral relationships between individual pixels. The SOM-RPM methodology has proven to be a robust technique that offers substantial advantages in this field.

This work will present several case studies across a broad range of sample types including:

1. Depth profiling of a multilayer double silver low emissivity glass coating which considers the entire mass spectrum at every voxel and illuminates interfacial mixing.
2. Depth profiling of polyaniline films highlighting structural flaws such as pinholes as well as subtle changes in chemistry caused by heat treatment.
3. Identification of subtle changes in 200nm extracellular vesicles due to inflammatory response in releasing cells.

9:30am **AS-ThM-7 Applications of Machine Learning in TOF SIMS Data Analysis: Classification and Quantitation**, *Lev Gelb, A. Walker*, University of Texas at Dallas

We present progress towards analysis of TOF SIMS data using machine learning (ML) methods. We posit that TOF SIMS is not more widely used because the data is too complex to be interpreted without expert knowledge, and investigate how machine learning might help. We primarily train models on simulated "big" data sets constructed by combining and/or resampling experimental spectra, with a focus on neural-network architectures. A particular interest is in uncertainty quantification and evaluation of the reliability of the models.

In the case of classification, models are constructed that can identify the type of material studied from a TOF SIMS spectrum. These are trained on libraries of reference data. Of particular interest in this application is the number of reference data that are required and how that varies with the number of material types to be distinguished.

We also consider determining the composition of a homogeneous sample consisting of two or more components for which reference spectra are available. That is, the sample consists of compounds which appear in some reference library, and the algorithm should identify what compounds are present and in what relative quantities. Factors complicating this kind of analysis include statistical noise, matrix effects, background, calibration error, and the likely case that the reference spectra were not taken under the same conditions (primary ion, ion energy, instrument manufacturer, etc.) as the data to be analyzed. Our approach is to generate a large number of simulated high-resolution TOF SIMS spectra of multicomponent samples, again based on TOF SIMS reference data. Complicating factors are also incorporated to varying degrees, and the resulting data sets are used to train the models. Model performance is then studied and related to spectrum quality, complexity and complicating factors.

9:45am **AS-ThM-8 AVS National Student Award Finalist Talk/ASSD Student Award Finalist Talk: Advancements in Tracer Diffusion Modeling with ToF-SIMS Depth Profiling**, *Nicolas Molina^{1,2}, A. Dolocan, G. Rodin, F. Mangolini*, The University of Texas at Austin

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) stands as a robust analytical characterization technique for determining the depth distributions of chemical moieties within solids. One of its main advantages is its capability to acquire and differentiate between the characteristic signals of isotopes of the same chemical element during a measurement. As such, stable isotopes have been employed as diffusion sources in tracer diffusion studies in a variety of fields, from energy storage to failure analysis. The standard methodology for these tracer diffusion experiments includes sample preparation, isotope dosing, ToF-SIMS depth profiling, and diffusion modeling. In this presentation, we highlight current shortcomings when modeling ToF-SIMS depth profiles in tracer diffusion experiments and

proposed improvements to overcome them, namely: 1) incorporation of the spatio-temporal experimental path of the diffusing isotope, which is crucial when ToF-SIMS acquisition and diffusion timescales are comparable (i.e., the depth profile cannot be considered frozen in time anymore) and allows for correcting the calculated transport constants, i.e., diffusivity (D) and surface exchange coefficient (Γ); 2) refinement of Fick's diffusion equations when the isotopic abundance (i.e., $^2\text{H} / (^1\text{H} + ^2\text{H})$) is used as a proxy for concentration instead of the isotope intensity (e.g., ^2H), as classical Fick's laws along with their boundary conditions do not hold for the isotopic abundance. These advancements in diffusion modeling open the path for the accurate use of ToF-SIMS for quantifying transport constants in tracer diffusion studies across a broad range of applications, including in those involving the use of ultrathin films.

11:00am **AS-ThM-13 ASSD Peter Sherwood Award Talk: Hybrid SIMS: Evolution of a SIMS Instrument Combining Time-of-Flight and Orbital Trapping Mass Spectrometry**, *Alexander Pirkl³*, ION-TOF GmbH, Germany
INVITED

Secondary ion mass spectrometry (SIMS) offers the possibility to acquire laterally resolved chemical information from submicron regions on inorganic and organic samples. However, SIMS analysers usually lack the required mass resolution, mass accuracy and high resolution MS/MS capabilities required for the thorough investigation of complex biological materials.

To specifically address the imaging requirements in the life science field and following the original idea of Prof Ian Gilmore (NPL), a Hybrid SIMS instrument was developed in a research project by IONTOF and Thermo Fisher Scientific in close cooperation with other partners of the 3D OrbISIMS project [1]. The instrument combines an Orbitrap-based Q Exactive HF mass analyser with a high-end ToF-SIMS system, providing a mass resolution $> 240,000$ and a mass accuracy < 1 ppm in conjunction with high lateral resolution cluster SIMS imaging capabilities. In this contribution we will put a spotlight on the different development steps involved in the initial project and later during its still ongoing evolution, always aiming at making this technology available to more applications.

[1] Passarelli, et al. Nature Methods volume 14, pp 1175–1183 (2017)

11:30am **AS-ThM-15 Multiplexing Analysis Using Microarray Plate for Fast Analysis by ToF-SIMS**, *Tanguy Terlier, C. Gramajo*, Rice University

Multiplexing analysis is a type of assay that permits to characterize complex samples in a single run analysis. Here, we used a computer-controlled CO₂ laser cutter for machining glass plates to pattern multiples 10-microns depth microwell. Among the most suitable characterization tool for producing multiplexing analysis, time-of-flight secondary ion mass spectrometry is a powerful surface analytical technique for providing detailed elemental and molecular information about the surface, thin layers, interfaces, and full 3D analysis of the samples.

Thanks to integrated large imaging capability by scanning an area of few mm², ToF-SIMS characterization permits a deeper exploration and a better knowledge of the organic and biological materials with complex chemical structures. ToF-SIMS produces hyperspectral images where each individual pixel contains a full mass-range spectrum. Spot areas can be selected by generating a region of interest area to treat each individually each sample. Our glass plate permits to create a library of 120 individual samples. After identification of the characteristic fragment ions, multivariate analysis is used to establish the correlation between the molecular ions and to classify the relationship between the samples.

Beyond the combination of the hyperspectral images with MVA techniques, we can elucidate the chemical composition of a large set of specimens to address complex analytical challenges or chemical reactions. The operation consists of performing a rapid single-scan ToF-SIMS analysis of the plate and then classifying the dataset for database-matching or quantification of the composition. In an initial study, a small number of monomers were characterized and then we used the dataset to discriminate the molecular signature as function of the functional groups. The method has been extended to several lipids to establish a library of characteristic fragments for further understanding of lipid deposition profiles from foreign body responses. A second study has consisted of identifying the surface composition of antibody-conjugated gold nanoparticles. Our final example will focus on developing methods for inhibiting asphaltene deposition.

To conclude, we will demonstrate through various case studies how multiplexing analysis using microarray plate for fast analysis by ToF-SIMS

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² AVS National Student Award Finalist

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can offer a rapid solution for building databases and establishing reference libraries of fragmented ions. In addition, this approach allows the classification and the correlation of chemical profiles from complex compounds, and potentially the quantification of mixture by dosing species ions from ToF-SIMS data.

11:45am AS-ThM-16 Exploring the Power of TOF-SIMS by Coupling Collision-Induced Dissociation with Surface-Induced Dissociation for Structural Analysis, *Jacob Schmidt, G. Fisher*, Physical Electronics USA

TOF-SIMS with kilo-electron volt collision-induced dissociation (CID) tandem MS is a powerful tool for compositional identification and structural elucidation of molecules, metabolites, and degradation products due to its ability to isolate ions of interest and provide further insights into its molecular structure and composition. TOF-SIMS tandem MS has been used to unambiguously verify analytes and to generate 2D and 3D maps of a brass corrosion inhibitor¹, to image organelles in single cells², and to discern the degradation pathway of OLEDs³.

In this presentation, we will explore the application of surface-induced dissociation (SID) coupled with CID, to assist in the confirmation of molecular assignments. In contrast to CID, which promotes cleavage at every molecular bond, SID is more subtle in that the bond cleavages result predominantly in the observation of functional group chemistry, as shown in Figure 1. The fragmentation energetics between SID and CID are distinct, even at the same kinetic energy, which leads to pronounced effects on mass calibration. This difference in fragmentation energies can have a significant effect on calibration, which we will address using isotopic abundancies to confirm compositional assignments.

1. M. Finšgar, *Corrosion Science*. **182** (2021) 109269.
2. P. Agüi-Gonzalez, et. al, *J. Anal. At. Spectrom.* **34** (2019) 1355-1368
3. K. Sawada, et. al, *SID Symp. Dig. Tec.* **54** (2023) 1291-1293

12:00pm AS-ThM-17 Dealing with Reproducibility and Replication Challenges in Surface Analysis: Sample Provenance Information, Parameter Reporting, and Cultural Issues, *Donald Baer*, Pacific Northwest National Laboratory

It has been increasingly recognized that in many areas of surface and materials science faulty data and analyses, along with sparse reporting of experimental and analysis details, complicate the ability of other researchers to assess and replicate published results. In the past several years, the surface analysis community has initiated multiple efforts to address these issues, mostly providing information and guidance to help researchers appropriately collect and analyze data. The status of some of these efforts will be reported during this talk with a focus on topics related to collecting sample provenance information, methods to facilitate parameter collection and reporting, and the importance of addressing cultural issues. The increased use of surface methods by both inexperienced analysts and use of the methods outside the surface analysis community contribute to the problem. Therefore a variety of guides, tutorials and helpful websites have been and are being prepared including two collections of papers on reproducibility challenges and solutions published in the *Journal of Vacuum Science and Technology A*, a series of Notes and Insight papers in *Surface and Interface Analysis*, with the objective of providing short focused discussions on important topics, a discussion of common XPS errors and parameter reporting in *Applied Surface Science Reports*, and the information in the websites *XPSlibrary.com* and *XPSOasis.org*. The ISO Committee TC201 on Surface Chemical Analysis is developing a standard on reporting information regarding preparation of samples for surface analysis. This information is important for a sample provenance record that provides a traceable history of samples undergoing analysis. Recent reports on the lack of information about instruments used for data collection and analysis will be partially addressed by new publications in *Surface Science Spectra* providing referenceable details about widely used commercial instruments along with descriptions of operator selected modes of instrument operation. Finally, these efforts will be effective only to the extent that the members of the community accept, use, and promote the use of these tools and concepts. Specifically, it is important that the culture of the community values and supports efforts to enhance research quality. There are important roles for reviewers, colleagues, educators, editors, professional societies, and granting agencies in identifying and addressing sloppy science.

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Room 117 - Session AS-ThA

Complementary Methods and Industrial Challenges

Moderators: Vincent Smentkowski, GE Research Center, Suntharampillai Thevuthasan, PNNL

2:15pm AS-ThA-1 ASSD Student Award Finalist Talk: Elucidating the Interaction Forces between Surface Nanobubbles and Nanoparticles, Daniela Miano¹, P. Bilotto, CEST GmbH, Italy; M. Valtiner, TU Wien, Austria
Efficient surface cleaning protocols are imperative across diverse industries to ensure product quality and performance. The new direction of nanoelectronics requires surfaces to be cleaned at the nanoscale. In the last decade, surface nanobubbles have been shown to remove nanoparticles from silicon wafers. [1] Nevertheless, the specific surface nanobubble-nanoparticle interaction has not been fully understood, calling for a deeper investigation.

We explore the formation and stability of surface nanobubbles by employing atomic force microscopy (AFM). After solvent/water exchange we characterize them in terms of topography and their interaction in different wettability and environment scenarios (i.e., change in solvent, nanoparticle types, gas concentration, and surface functionalization). The presence of NBs can lead to localize changes in wettability, roughness, and chemical reactivity.

Managing the balance between enhanced cleaning and surface potential is crucial. Over time, this alteration may impact the substrate's integrity or alter its performance characteristics.

Interestingly, we observe the formation of nanoholes, which we interpret in terms of short range forces (DLVO theory) and chemical equilibrium in confinement. The latter takes inspiration from *pressure solution* as described in geology. It helps identify the physical and chemical interactions occurring when nanoparticle detachment from the substrate. [2]

Our research work aims to describe solid-liquid interface, with particular interest to the phenomena correlate the interactions force between surface nanobubble-nanoparticles and surface and nanoparticles-surface. Research on surface nanobubble and the study of their possible application is necessary because there is not a unified vision in the scientific community. The results can impact both the scientific and industrial categories, by addressing respectively unsolved interactions at the nanoscale and upscaling nano-cleaning processes at the macroscale.

[1] S. Yang, & A. Duisterwinkel, A. (2011). Removal of Nanoparticles from Plain and Patterned Surfaces Using Nanobubbles. *Langmuir*, 27(18), 11430–11435. doi:10.1021/la2010776;

[2] K. Kristiansen, M. Valtiner, G.W. Greene, J.R. Boles, J.N. Israelachvili (2011). Pressure solution - The importance of the electrochemical surface potentials. doi:10.1016/j.gca.2011.09.019

2:30pm AS-ThA-2 A Correlative Microscopy Platform for In-Situ AFM-SEM-EDS, Kerim T. Arat, W. Neils, S. Spagna, Quantum Design Inc.

In-situ correlation of AFM-SEM techniques implemented in a highly integrated tool offers the complementary strengths of two different imaging modalities without the inherent complications of sample transfer. This is not only a significant convenience for researchers but also ensures a high confidence in correlation accuracy and eliminates the risk of sample contamination and alteration during the sample transfer.

Previously, we have developed a correlative microscopy platform based on AFM-SEM [1]. These techniques can map the surface in high resolution and the trunnion, with up to 80° tilt capability, allows monitoring of process quality such as tip measurement or monitoring tip sample interaction. However, none of these can measure the elemental composition of the material.

We have extended the capabilities of the correlative platform with an energy-dispersive X-ray spectrometer (EDS) to extract the elemental information from the sample. The spectrometer is based on a state-of-the-art silicon drift detector [2], which provides high energy resolution (< 133 eV, Mn-Kα). Its unique graphene window offers better transmission, especially at the lower energy range, allowing elemental detection down to

carbon. The EDS elemental identification algorithm uses a background subtraction method and compares the resulting spectra to reference datasets based on the NIST database [3]. Both hardware and software integration allow correlation of elemental information with the other imaging modalities that the tool can provide (see the supplementary document) where one can superimpose topography and elemental information.

Integration of the X-ray detector adds a significant analysis capability to AFM-SEM techniques applicable to a diverse range of materials such as metals, alloys, ceramics, and polymers. With this addition of EDS, researchers can obtain in-situ correlation of high-resolution, localized elemental information with high-resolution lateral and vertical topographical information, without the complications of sample transfer.

[1] A. Alipour et al., *Microscopy Today* 31 (2023), p. 17-22. doi: 10.1093/mictod/qaad083

[2] D. E. Newbury and N. W. M. Ritchie, *Journal of Materials Science* 50 (2015), p. 493-518. doi: 10.1007/s10853-014-8685-2

[3] D. E. Newbury and N. W. M. Ritchie, *Scanning Microscopies* 9236 (2014), p. 9236OH. doi: 10.1117/12.2065842

2:45pm AS-ThA-3 Coincident XPS, Raman and SEM Analysis of Additive Manufacturing Devices, Mark Isaacs, University College London, UK; D. Morgan, Cardiff University, UK; A. Leung, K. Kim, S. Bhagavath, University College London, UK

Additive manufacturing processes are a keenly investigated methodology for the preparation of sophisticated devices for a multitude of technologies, including catalysis, electronics and sensors. At the heart of the functionality of these systems often lies the surface and interfacial properties of the resultant materials. In order to develop a holistic understanding of the eventual nature of these devices, and for the complete assessment of favourable printing parameters, oftentimes a multitude of characterisation methods is required. Coincident analysis of surface analysis techniques such as XPS, SEM, REELS and UPS - along with additional complementary techniques such as Raman spectroscopy - permits a wealth of understanding around the physical, chemical and electronic properties of printed tracks and leads to an overall optimisation of system parameters to develop highly specific and tuneable materials. In this work, we study a range of printing parameters for the deposition of MoO₃ tracks onto a copper support - a material with promising applications in the electrocatalytic reduction of CO₂. Using XPS, linked with SEM/EDX via a CISA (Correlative Imaging and Surface Analysis) Workflow and Raman spectroscopy, we investigate a range of printing parameters in order to determine favourable properties for the creation of phase interfaces understood to be active for electrocatalytic applications. Chemical and electronic properties are also investigated through complimentary surface analysis by REELS and UPS.

3:00pm AS-ThA-4 Analysis of Cu-Ag and Ni-Pt High Throughput Survey Results, Kyle Dorman, N. Bianco, R. Kothari, M. Kalaswad, C. Sobczak, S. Desai, J. Custer, S. Addamane, M. Jain, A. Hinojos, F. DelRio, B. Boyce, R. Dingreville, D. Adams, Sandia National Labs

Nanocrystalline thin films feature the potential for enhanced or altered material properties compared to their bulk single crystal counterparts. Recent studies on Pt-Au binary thin films have emphasized the role of grain boundary character in successful solute stabilization of otherwise thermally unstable nanocrystalline systems (C. M. Barr et al., *Nanoscale*, 2021), and means of high-throughput combinatorial synthesis (McGinn, *ACS Comb. Sci.*, 2019) have been developed to complement automated characterization and modern simulation capacity. To further develop our understanding and suite of tools, and to step beyond the most noble alloy into more economically practical material systems, compositional surveys of Cu-Ag and Ni-Pt were performed in search of optimized material properties and greater comprehension of nanocrystalline systems. Facilitated by a fixed substrate and photolithography, a simultaneous co-sputtered deposition of each pair of elements with pulsed DC magnetron methods directing single element sources creates a varied atomic composition across 112 samples on a single 150 mm diameter wafer. A series of such depositions, varying the gun-tilt angle and power at each cathode, allows swift examination of nearly the full range of alloy compositions. Wavelength Dispersive Spectroscopy, Atomic Force Microscopy, X-ray Diffraction, X-ray Reflectivity, sheet resistance, optical profilometry and nanoindentation were employed for automated mapping analysis. The binary collision Monte Carlo program SiMTra (D. Depla et al., *Thin Solid Films*, 2012) assisted with the deposition design to minimize the necessary quantity of sample batches, and enabled analysis of the

¹ ASSD Student Award Finalist

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energetic and compositional properties of the wafer at deposition with respect to the resultant hardness, modulus, film density, crystal texture and resistivity. This permits specification of desirable processing conditions in relation to exemplary and underperforming films. Accompanied by exploration of the strengths and weaknesses of the dataset, and the means to improve further such surveys.

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3:15pm AS-ThA-5 Characterization of Functional Surface Modifications in Medical Devices, *Andrew Francis, A. Rafati, A. Belu*, Medtronic, Inc.

Surface modifications provide important functionality for medical devices, such as increased lubricity, improved hemocompatibility, and localized drug delivery. Characterization of these modifications is essential to understanding and controlling their interactions with a patient. Here, the development and characterization of new functional surface modifications for medical devices is reported with several examples shown. In particular, the spatial-chemical distribution and functional testing of a new biomimicry surface modification will be highlighted in combination with key clinical results. A range of analytical techniques (SEM/EDS, TOF-SIMS, XPS, and Raman spectroscopy) and biochemical methods and assays (blood loop model, TAT, etc.) will be discussed.

3:30pm AS-ThA-6 XPS Study of ZrN as a Barrier to Silver Migration in TRISO Fuels, *Jeff Terry*, Illinois Institute of Technology

We have measured simulated TRISO Fuel model structures of SiC and ZrN with and without a 2 nm carbon capping layer. We have used both Sputter Depth Profiling with conventional X-ray Photoemission (XPS) and Ambient Pressure X-ray Photoemission Spectroscopy (APXPS) to explore the reactivity of these layers with both Ag and H₂O. One set of the samples that were depth profiled were measured at room temperature. Another set was annexed to 500 °C and then cooled to room temperature before profiling. The samples measured with APXPS were exposed to 1 mbar of H₂O exposure and annealing up to 500 °C. The exposure was done in a near ambient pressure cell within the XPS system. High resolution scans of the Ag 3d, Zr 3d, O 1s, Si 2p, C 1s and N 1s region were collected and the peaks were fit to identify the chemical species as it is being exposed and annealed. The fitting was performed using our Artificial Intelligence analysis package XPS Neo. This study shows that materials used in TRISO fuel (SiC and ZrN) have a strong reaction to water and high temperature and having a barrier layer of carbon to can effectively prevent oxidation of the materials. The Ag is effectively stopped by the ZrN layer. Adding a layer of ZrN may prevent exposure to workers during shutdowns.

3:45pm AS-ThA-7 Surface Properties of Actinide Dioxide and Their Effect on Reactivity, *Enrique Batista, G. Wang, P. Yang*, Los Alamos National Laboratory

Actinide compounds, especially actinide oxides, play a critical role in many stages of the nuclear fuel cycle. The behavior of these materials under different conditions dictates aspects from crystal growth to disposal of spent fuels, and much of those properties start at the surface. In that way, catalytic reactions that can lead to unstable storage conditions stemming from surface interactions with environmental species. Similarly, the morphology and structure is dictated environmental conditions and the reactivity of the incipient solid to the species present in solution. We have recently been focusing on surface properties induced by the presence of surface defects and surface interactions with environmental and non-environmental molecules. In this presentation we discuss the effect of surface defects in the reactivity and catalytic properties of the different exposed surfaces. Examples of reactions catalyzed by actinide surfaces to be discussed include water oxidation and nitrogen reduction to ammonia. Since these interactions can be deleterious, approaches to prevent them without affecting the desired properties of the material will also be discussed. We present results of these studies for a series of actinide dioxides (AnO₂).

4:00pm AS-ThA-8 Degradation Analysis of Bitumen Using XPS, *Nirmalya Karar*, National Physical Laboratory, India; *S. Kar*, CSIR-CRRI, India

In this presentation, we shall discuss about the degradation of bitumen as observed using XPS. It was initially thought that XPS could not be done on such samples as it is an oil based product with a non-negligible vapor pressure. We use 2 different bitumen grades for our analysis. Road Engineers denote them as VG-10 and VG-30 respectively. Different old used bitumen samples of known provenance were extracted from Indian roads for this analysis and compared with control samples obtained from an

Indian oil company. The primary elements present were C (C1s), S (S2p) and O (O1s). N(1s), Pb (Pb4f) or Ni (Ni2p) were not seen in these samples. We shall show how these elemental peaks change under different conditions as compared to the control samples. The significance or importance of our studies on the local economy is due to the tropical weather conditions present in South Asia, e.g. high rainfall, high temperatures, heavy sunshine for most parts of the year, heavy traffic loads, and large differences in daily maximum and minimum temperatures on many parts of the country, leading to relatively faster degradation of bitumen-asphalt based roads, as opposed to similar roads in colder countries. So, a road construction methodology that may be suitable and quite successful in moderate or cold climatic conditions may not necessarily be as successful for tropical countries.

4:15pm AS-ThA-9 High-Efficient Bifacial Ge-incorporated Sb₂Se₃ Photovoltaic Devices Enabled with Cu₂O Back Buffer, *Sanghyun Lee, K. Price*, University of Kentucky

Antimony Selenide (Sb₂Se₃) thin-film solar cells have gained attention as third-generation photovoltaic devices with promising properties. With a bandgap of 1.1 eV, it has a high absorption coefficient at visible light (>10⁵ cm⁻¹), good carrier mobility (<15 cm²/Vs), long carrier lifetime (<67 ns). Additionally, the simple binary nature of Sb₂Se₃, along with its high vapor pressure and low melting point, makes it suitable for various cost-effective deposition techniques. The versatility of Sb₂Se₃ thin-films has led to extensive research into their composition and the integration of different elements for a range of uses. Specifically, incorporating Germanium into Sb₂Se₃ (Ge-Sb₂Se₃) has shown promise as an effective polycrystalline absorber, especially when the Germanium content is maintained below 15%.

Enhancing the performance of polycrystalline Sb₂Se₃ devices could be achieved by capturing light on both the front and back sides through a bifacial device design. However, the advancement of bifacial devices in thin-film photovoltaic technologies has been limited due to their short carrier lifetimes (<100 ns), especially when compared to polysilicon-based devices. For example, the highest efficiencies recorded for rear-side illumination are 9.2% for CIGS, 8.0% for CdTe, and 9.0% for Kesterite solar cells. Research into optimizing bifacial photovoltaic structures is ongoing and a key is to select a transparent back buffer layer and a transparent conducting back contact, adjusting the thickness and doping concentration to enhance the bifaciality factor (efficiency ratio of rear-to-front illumination).

In this study, we have investigated the feasibility of developing bifacial Ge-Sb₂Se₃ devices, beginning with the creation of Ge-Sb₂Se₃ absorber thin films and proceeding to assessing their optical characteristics. These characteristics were then employed as critical input parameters for the computational modeling and simulation of the bifacial device structure. Utilizing in-house MATLAB modeling suites connected to external Sentaurus TCAD simulators, we introduced innovative bifacial device designs aimed at enhancing device efficiency and further refined these models by adjusting a set of parameters. After carefully selecting a Cu₂O back buffer layer, the best efficiency of front-side illumination is 19.7 %, and Voc is 744.4 mV, Jsc is 40.14 mA/cm², and FF is (66.1 %). For the rear-side illumination, efficiency is 13.0 %, Voc is 724.5 mV, Jsc is 31.6 mA/cm², and FF is 56.7 %. All in one, the bifaciality factor of Ge-Sb₂Se₃ devices was 66 %.

Applied Surface Science

Room Central Exhibit Hall - Session AS-ThP

Applied Surface Science Poster Session

AS-ThP-1 Advances in the Chemical Composition Quantification of Surface and Volume Using HAXPES Data, Dulce-Maria Guzman-Bucio, CINVESTAV-Unidad Queretaro, Mexico; *J. Huerta-Ruelas,* CICATA Queretaro, Mexico; *O. Cortazar-Martinez,* CINVESTAV-Unidad Queretaro, Mexico; *D. Cabrera-German,* Universidad de Sonora, Mexico; *J. Torres-Ochoa,* Universidad Politecnica de Juventino Rosas, Mexico; *A. Carmona-Carmona,* CINVESTAV-Unidad Queretaro, Mexico; *O. Ceballos-Sanchez,* Universidad de Guadalajara, Mexico; *W. Limestall, Z. Lee, M. Warren, J. Terry,* Illinois Institute of Technology; *A. Herrera-Gomez,* CINVESTAV-Unidad Queretaro, Mexico

In recent decades, HAXPES has gained scientific and technological relevance. This method offers several advantages, including the capability to analyze both the surface and bulk of materials. It allows for the analysis of buried layers without requiring the removal of top surface layers by ion sputtering, thereby eliminating sample damage. Additionally, the interference with Auger signals decreases. However, there are significant challenges for quantitatively interpreting the data.

As with XPS, assessing chemical composition with HAXPES requires differential photoelectric cross-sections. For HAXPES, it is essential to consider the increasing relevance of non-dipole terms.

This study presents a summary of the requirements and challenges associated with employing HAXPES data for chemical composition analysis of iron oxide samples. Additionally, we provide insights into the application of a MultiLayer-Method to analyze multilayered films using photoemission data from a partially oxidized iron film as the X-ray crossed the iron K edge. These experiments were carried out at Beamline 10-ID-B at the Argonne National Laboratory.

AS-ThP-2 Basic Aspects of the Asymmetry of Lineshapes in Photoemission Spectra Caused by a Cascade of Excitations of Fermi-Level Electrons, A. Dutoi, University of the Pacific; **Alberto Herrera-Gomez,** Cinvestav, Mexico; **D. Guzman-Bucio,** CINVESTAV-Unidad Queretaro, Mexico

The effect of cascade excitations of Fermi-level electrons on the lineshape of photoemission spectra was treated by Doniach and Sunjic (DS) in 1970.¹ Their derived lineshape has many issues such as its lack of integrability and failure to closely reproduce experimental data.² We analyze this problem using a formalism rooted only in the basic quantum mechanics of resonances with a minimalist diagrammatic veneer to categorize the many-body of processes (Tougaard losses, plasmons/hole-shielding, multiplet structure, and perhaps the Shirley background). The accounting for these processes can be done with varying levels of rigor, from simple consideration of energy scales, oscillator strengths, and couplings, through to *ab initio* calculations of matrix elements. A density-matrix formulation in the many-body space can be applied to remove spurious interferences of states that have ill-defined/incoherent relative phases (differ from shot to shot, due to pulse noise, sample inhomogeneities, temperature, etc.). In our work, we will apply the simplest level of semi-quantitative analysis to propose possible alternatives to the problematic DS lineshape. For example, an incoherent superposition of exponential decay in time yields a lineshape that is asymmetric but integrable.

¹ S. Doniach and M. Šunjic, "Many-electron singularity in X-ray photoemission and X-ray line spectra from metals," *Journal of Physics C: Solid State Physics* **3**, 285–291 (1970).

² A. Herrera-Gomez, D.M. Guzman-Bucio, A.J. Carmona-Carmona, O. Cortazar-Martinez, M. Mayorga-Garay, D. Cabrera-German, C.A. Ospina-Ocampo, B.V. Crist, and J. Raboño-Borbolla, "Double Lorentzian lineshape for asymmetric peaks in photoelectron spectroscopy," *Journal of Vacuum Science & Technology A* **41**(4), (2023).

³ A. Herrera-Gomez, D. Cabrera-German, A. D. Dutoi, M. Vazquez-Lepe, S. Aguirre-Tostado, P. Pianetta, D. Nordlund, O. Cortazar-Martinez, A. Torres-Ochoa, O. Ceballos-Sanchez, and L. Gomez-Muñoz, "Intensity modulation of the Shirley background of the Cr 3p spectra with photon energies around the Cr 2p edge," *Surface and Interface Analysis* **50**, 246–252 (2018).

AS-ThP-3 XPS Study of the Initial Oxidation of Iron for Ultrathin and Thick Films, Orlando Cortazar-Martinez, J. Torres Ochoa, J. Fabian-Jacobi, J. Raboño Borbolla, A. Herrera-Gomez, CINVESTAV-Unidad Queretaro, Mexico
We studied the initial stages of oxidation of ultrathin and thick iron films on silicon. Clean films were exposed to a controlled ultra-pure oxygen atmosphere with varying gas dosages at room temperature. The characterization was done with angle-resolved XPS [1]; the data was analyzed using robust analysis techniques including the block approach [2] and simultaneous fitting, as well as background modeling with the active approach, Shirley-Vegh-Salvi-Castle (SVSC), and the Two-Parameter Tougaard background [3].

While thick films oxidize in a layer-by-layer fashion, thin films exhibit oxidation by clusters or islands. The multilayer method (MLM) was employed to quantify the ultrathin films' chemical composition and structure. In both cases, Fe₂O₃ is the oxide composition.

This work was partially financed by Proyecto Fronteras 58518, Conahcyt, Mexico.

[1] A. Herrera-Gomez, O. Cortazar-Martínez, J.F. Fabian-Jacobi, A. Carmona-Carmona, J.G. Raboño-Borbolla, M. Bravo-Sanchez, J.A. Huerta-Ruelas, A self-consistent multiple-peak structure of the photoemission spectra of metallic Fe 2p as a function of film thickness, *Surface and Interface Analysis* **52** (2020) 591–599. <https://doi.org/10.1002/sia.6796>.

[2] A. Herrera-Gomez, M. Bravo-Sanchez, O. Ceballos-Sanchez, M.O.O. Vazquez-Lepe, Practical methods for background subtraction in photoemission spectra, *Surface and Interface Analysis* **46** (2014) 897–905. <https://doi.org/10.1002/sia.5453>.

[3] S. Tougaard, Universality classes of inelastic electron scattering cross sections, *Surf. Interface Anal.* **25** (1997) 137. [https://doi.org/10.1002/\(SICI\)1096-9918\(199703\)25:3<137::AID-SIA230>3.0.CO;2-L](https://doi.org/10.1002/(SICI)1096-9918(199703)25:3<137::AID-SIA230>3.0.CO;2-L).

AS-ThP-4 Rapid Assessment of Detector Linearity and Deadtime Correction for XPS Instruments, Benjamen Reed, A. Shard, National Physical Laboratory, UK

Confidence in the intensity scale of a photoelectron spectrometer is vital for quantitative analysis of photoelectron spectra. This is because the integrated area under a core level peak is proportional to the atomic fraction of that element in the sample. Sample dependent factors aside, the XPS analyst must calibrate for the intensity response (or transmission function) of their analyser, which is largely a result of electrostatic lens column and is unique for each instrument. However, even before a spectrum is acquired, there must be confidence that the measured count rate of the analyser's detection system is correct. For example, at high count rates, the detector may exhibit a non-linear response that significantly effects the measured count rates, and therefore the peak intensities from which atomic fractions are calculated. At even higher count rates, detector saturation may occur. So, although it is tempting to conduct XPS measurements with increased count rates (e.g. by increasing X-ray emission with high throughput electrostatic lens modes and collimation settings) with the intent to improve signal-to-noise and reduce experiment times, this approach is stymied by the limits of the detection system itself.

Recently an interlaboratory study on XPS intensity calibration was organised by the National Physical Laboratory (NPL) under the auspices of the Versailles Project on Advanced Materials and Standards (VAMAS). In the interlaboratory study, a number of datasets on sputter cleaned gold were submitted that exhibited evidence of detector non-linearities. It appears then, that awareness of this limitation of photoelectron detectors may not be universally known throughout the XPS users' community. Therefore, we shall briefly introduce these concepts and then present a straightforward method for rapidly assessing the linearity and deadtime correction for photoelectron spectrometer detectors which is based on the spectrum ratio method from Annex A of ISO 21270 ("Surface chemical analysis — X-ray photoelectron and Auger electron spectrometers — Linearity of intensity scale").

Thursday Evening, November 7, 2024

AS-ThP-5 ASSD Student Award Finalist Talk: Dry and Wet Etching of Single-Crystal AlN, Hsiao-Hsuan Wan¹, C. Chiang, J. Li, University of Florida; N. Al-Mamun, A. Haque, Penn State University; F. Ren, S. Pearton, University of Florida

The dry etching of high crystal quality c-plane AlN grown by Metal Organic Chemical Vapor Deposition was examined as a function of source and chuck power in Inductively Coupled Plasmas of Cl₂/Ar or Cl₂/Ar/CHF₃. Maximum etch rates of ~1500 Å•min⁻¹ were obtained at high powers, with selectivity over SiO₂ up to 3. The as-etched surfaces in Cl₂/Ar/CHF₃ have F-related residues, which can be removed in NH₄OH solutions. The Al-polar basal plane was found to etch slowly in either KOH or H₃PO₄ liquid formulations with extensive formation of hexagonal etch pits related to dislocations. The activation energies for KOH or H₃PO₄-based wet etching rates within these pits were 124 and 183 kJ/mol, respectively, which are indicative of reaction-limited etching.

AS-ThP-6 Multitechnique Analysis of Ultrathin Films for the Photocatalytic Production of Sustainable Aviation Fuels, Mark Isaacs, University College London, UK; L. Durndell, University of Plymouth, UK; C. Parlett, University of Manchester, UK; C. Drivas, Cardiff University, UK

In the search for technologies by which to reduce the overreliance on traditional fossil fuel based transport, the utilisation of biomass derived feedstocks to produce aviation fuels represents an exciting avenue for minimising the carbon footprint of global travel. Developing new materials, and improving and optimising the performances and activities of these materials requires a fundamental understanding of the physical, chemical and electronic properties down to the nano-domain - particularly when considering some of the more sophisticated synthetic protocols employed in advanced nanomaterials such as surface modifications via ultra-thin films, galvanostatic interaction depositions, formation of Schottky junctions and more. X-ray photoelectron spectroscopy (XPS), and surface science in general, is ideally suited to extracting directly relevant information about these properties and, when combined in a coincident manner, develop a completely holistic understanding of how nanomaterial synthesis parameters may be controlled to imbue fine control over the resultant properties - and understand how these may impact upon catalytic activities. In this work, we investigate a series of ultra-thin layers of titania deposited onto the surface of a high surface area silica and correlate material properties with the catalytic performance in the acetalisation of furfural into 2,5-Bis(2-furylmethylene) cyclopentanone. Comprehensive chemical, electronic and structural analysis is performed using a combination of correlative XPS, REELS, UPS, Raman and ISS, and mapped with catalytic performance in the presence and absence of stimulating light.

AS-ThP-7 Probing the Adhesive / Substrate Interface Using Back Side Sims Profiling Facilitated by Releasable Thin Metal Films, Paul Vlasak, S. Altum, T. Fielitz, J. Beebe, Dow Chemical Company

Depth profiling using secondary ion mass spectrometry (SIMS) or other surface sensitive methods is an attractive strategy for studying cured adhesive or sealant compositions near their interfaces with substrate materials to take advantage of the extraordinary depth resolution of these methods. A classic problem with this approach is that a poor performing sample may exhibit adhesive failure, so that the interface of interest can be easily exposed and ideally presented to the analyzer, while the exemplary sample exhibits cohesive failure, and the interface of interest remains hopelessly buried beneath an irregular layer of adhesive. Here we present one approach to facilitate back side profiling from the substrate side, allowing analysis of the interface of interest without requiring adhesive failure at the interface. In the demonstrated approach, a 20 nm thick layer of aluminum was deposited on a sacrificial polymer film. The adhesive of interest was cured against the aluminum surface under varying environmental cure conditions. The polymer film was then peeled away, leaving the thin aluminum layer intact on the adhesive. SIMS depth profiles through the aluminum into the adhesive allowed a direct comparison of near surface chemical composition, revealing different distributions of formulation components depending on cure conditions.

AS-ThP-8 Probing the Effects of Surface Chemistry on Quality Factor and Coherence Times of Superconducting Radio Frequency Cavities and Qubits, Adam Clairmont, J. Lee, A. Murthy, FermiLab

Understanding the chemistry of both surface and bulk properties is important for improving the performance of superconducting radio frequency (SRF) cavities and superconducting qubits. Utilizing state-of-the-art material characterization tools, researchers can better understand the

impact subtle changes in chemistry have on quality factors and coherence times of such devices. Fermilab's Material Science Laboratory co-operated by the Applied Physics and Superconducting Technology Directorate and Superconducting Quantum Materials and Systems Center houses a custom-built x-ray photoelectron spectroscopy (XPS) instrument that was designed with the characterization of SRF cavities and qubits in mind.

A monochromatic silver anode accompanies the standard monochromatic aluminum anode. This allows the researcher to increase their information depth from 9-10 nm (Al) to 17-20 nm (Ag), access a greater number of core levels, and to shift Auger transitions to avoid possible peak overlaps. Using a small spot lens mode, XPS mapping can be done with <30um achievable spatial resolution. If increased spatial resolution is needed, the electron source can be used for Auger or scanning Auger microscopy with sub-micron spatial resolution. Band gaps can be analyzed with the Helium (I and II) ultraviolet source. An argon gas cluster ion beam with selectable cluster size, monatomic-3000 Ar ions per cluster, allows rapid low-damage sputtering. A high-pressure chamber can reach temperatures approaching 1073 Kelvin (K) while also introducing gasses such as nitrogen, oxygen, hydrogen, carbon dioxide, and various inert gasses up to pressures of 20 bar. As this chamber is directly attached to the system, samples can be transferred into the load lock and into the analysis chamber following heat treatments without exposure to air. Finally, a liquid helium manipulator is coupled with an e-beam heater for *in situ* characterization from less than 15K to 1073K.

This unique tool has enabled a wide variety of scientific studies that have improved our understanding of sources limiting the performance of SRF cavities as well as superconducting qubits and I will present results from some of these efforts.

AS-ThP-9 Electronic Structure in a Transition Metal Dipnictide TaAs₂, S. Regmi, Idaho National Laboratory; Arun Kumar Kumay, M. Neupane, University of Central Florida

The family of transition-metal dipnictides (TMDs) has been of theoretical and experimental interest because this family hosts topological states and extremely large magnetoresistance (MR). Recently, TaAs₂, a member of this family, has been predicted to support a topological crystalline insulating state. Here, by using high-resolution angle-resolved photoemission spectroscopy (ARPES), we reveal both closed and open pockets in the metallic Fermi surface and linearly dispersive bands on the (-201) surface, along with the presence of extreme MR observed from magneto-transport measurements. A comparison of the ARPES results with first-principles computations shows that the linearly dispersive bands on the measured surface of TaAs₂ are trivial bulk bands. The absence of symmetry-protected surface state on the (-201) surface indicates its topologically dark nature. The presence of open Fermi surface features suggests that the open-orbit fermiology could contribute to the extremely large MR of TaAs₂.

AS-ThP-10 Misunderstandings in Field Electron Emission Theory: The Great Fowler-Nordheim Hoax, Richard Forbes, University of Surrey, UK

Field electron emission (FE) is electrostatic-field-induced electron emission from a material surface. Many vacuum-based technologies involve FE. This Poster corrects a widely held misconception about FE theory.

In 1928, *qualitatively* correct theories of FE as wave-mechanical transmission were given by Oppenheimer and by Fowler and Nordheim (FN), using different approaches. But FN also used Fermi-Dirac statistics to explain weak FE temperature dependence near 300 K. Thus, FN get credit for explaining FE. In fact, FN's paper is flawed both theoretically and numerically. Image-charge effects were much under-estimated and there was a separate numerical error by about 10¹⁵. The numerical error was corrected by Stern et al. in 1929. The image-charge error was found by Nordheim later in 1928, but he then made a new error when using complete elliptic integrals. Nordheim's mistake was corrected by Burgess, Kroemer and Houston in 1953. In 1956, Murphy and Good (MG) developed revised FE theory that gave much higher current densities (100 times or more) than Stern et al. Unfortunately, many later authors called MG's theory the "Fowler-Nordheim equation".

In the 1990s, interest in displays brought many new researchers into FE. It seems many did not realise that the term "Fowler-Nordheim equation" often referred to the 1956 MG FE equation rather than the 1920s-era equations. More confusion was caused by the use of a simplified ("elementary") version of the 1920s-era equations to extract the electrostatic parameter "field enhancement factor" from experiments. This is now widely done. But if the elementary FE equation is used to predict current densities, or extract emission areas, then errors of order 100 or more arise, as compared with 1956 MG FE theory. Thus, modern FE

¹ ASSD Student Award Finalist

technological literature is highly misleading, especially for non-experts. Hundreds of papers give the elementary FE equation as FE theory, and cite the FN 1928 paper as justification. This paper has over 8000 citations, but few draw attention to its theoretical weaknesses. Hundreds of authors have been "hoaxed" by misleading FE literature, and then perpetuate the hoax.

When developing new types of high-quality electron source, or studying the role of FE in electrical breakdown, it is misleading to publish/use an equation that underpredicts emitter performance by 100 times or more. When extracting emission-area estimates for R&D use, it is unhelpful to use an equation that over-predicts area by 100 times. A good remedy uses a modern version of the 1956 equation, calls it the "Murphy-Good FE equation", and cites a modern FE research handbook.

AS-ThP-11 Analysis of High-k Metal Stacks by Hard X-Ray Photoelectron Spectroscopy Under Bias, Anja Vanleenhove, T. Conard, IMEC Belgium; D. Desta, H. Boyen, Hasselt University, Belgium

While the replacement of SiO₂ by high-k materials started in the early 2000s, the need for a deep knowledge of band-energies in complex high-k stacks is a hot topic in research and development in the advanced CMOS industry.

Although XPS is most commonly used as a technique to study the chemical composition of the top surface and thin layers plus interfaces in the top of the stack, Kumar *et al.* have demonstrated how the technique could be used to examine band-energies in high-k metal stacks with the established XPS using Al K α radiation. For XPS using Al K α , the analysis depth is limited to the top 5-10 nm. With the recently developed laboratory based hard X-ray photoelectron spectrometers (HAXPES) the path is opened to the analysis of thicker stacks and deeper buried interfaces (20-50 nm).

In this work, we will demonstrate the use of HAXPES under bias to examine relevant high-k metal stacks and illustrate that, as is the case for all other analysis techniques, this technique has its own limitations as well.

The examined samples and measurement set-up are modelled to enable an effective biasing across the stack while executing the HAXPES measurement. The samples consist of Si/SiO₂ substrates topped with high-k materials Al₂O₃ and HfO₂ which are covered with TiN. The sample matrix is designed to study different stack orders of the high-k materials as well as different high-k layer thicknesses. HAXPES measurements are executed on the HAXPES Lab of Scienta Omicron, a tool which combines a high flux monochromated Ga K α X-ray source of 9252.1 eV with an Al K α X-ray source of 1486.6 eV.

Reference: P. Kumar *et al.*, "Development of X-ray Photoelectron Spectroscopy under bias and its application to determine band-energies and dipoles in the HKMG stack," *2018 IEEE International Electron Devices Meeting (IEDM)*, San Francisco, CA, USA, 2018, pp. 17.6.1-17.6.4, doi: 10.1109/IEDM.2018.8614554.

AS-ThP-12 XPS Analysis of Plasma Exposed TiB₂ and ZrB₂ Substrates, Harry Meyer, L. Nuckols, C. Parish, J. Rapp, ORNL

Deuterium and hydrogen plasma exposures were performed on ultra-high temperature ceramics TiB₂ and ZrB₂ using the PISCES-RF linear plasma device as early screening tests for first wall, plasma facing material applications. These ion plasma exposures were performed using 40 eV ion energies at 240, 525, and 800 °C sample temperatures and 90 eV ion energies at 240 °C sample temperatures to analyze TiB₂ and ZrB₂ sputtering and surface morphology evolution behavior. Post-plasma exposure chemistry characterization of the near surface (< 50 nm) region using x-ray photoelectron spectroscopy (XPS) shows transition metal enrichment, indicating boron preferential erosion, and resulting in reduced total sputtering yields compared to predicted assuming stoichiometric sputtering. Transition metal to boron fractions vary with plasma exposure temperature under the 40 eV ion energy exposure at different temperatures; metal enrichment is maximized at 800 °C and then minimized at 525 °C. Sputtering yield measurements of the 40 eV ion energy plasma exposed samples show that the samples with greater metal surface enrichment have lower sputtering yields, likely due to the rougher surfaces of the more metal-enriched samples leading to higher instances of prompt redeposition processes. XPS data was acquired on the as-exposed TiB₂ and ZrB₂ samples. Depth profiles were then done to track the amounts of T (or Zr) and B as a function of Ar-ion sputter depth. Data was finally acquired on the well sputtered sample surfaces. This abstract has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy.

AS-ThP-13 Update on Using Different Instruments on the Same Sample and Getting Similar Results, Lyndi Strange, D. Baer, M. Engelhard, V. Shuthanandan, Pacific Northwest National Lab; A. Shard, National Physical Laboratory, U.K.

Literature analyses indicate growing use of XPS in multiple disciplines and increasing observations of faulty analysis. To ensure reliable results, detailed attention is required to acquisition and analysis. Our laboratory has instruments from three vendors, and it may be necessary to collect data from the available instrument. Users often export data for analysis using alternative software. It is useful to know the consistency of data collected on "identical" samples on different systems and analyzed using "native" (or blind) data export to other software packages. This paper describes what we thought was a "simple" test of data collection on three different systems and analysis using the native software for each system and analysis when naively exported to a non-native software package. Copper foil was the test specimen from which survey and high-resolution spectra were collected using Kratos Axis DLD Ultra, Thermo-Fischer NEXSA, and Phi Quantera spectrometers. Using both survey and narrow window data, the analyses included: i) comparison of Cu 3p and Cu 2p peak ratios, ii) Cu 3p and Cu 2p atom ratios using native software and iii) when exported to CasaXPS. We also compared the wide scan spectra shapes to the ideal Cu spectra provided by the National Physical Laboratory to obtain an approximate instrument response function. Although simple in concept, these comparisons were found to be less than straightforward. High count rate survey spectra ratioed to the ideal spectra produced unexpected variations in the instrument response functions. These ratios made more sense when count rates were reduced by lowering the X-ray intensity or decreasing the pass energy. Cu 3p and Cu 2p peak ratios were determined using peak intensities after removal of an iterated Shirley background between 58.0 eV and 91.0 eV for Cu 3p and 920.0 eV to 970.0 eV for Cu 2p. Because of variations in the instrument geometry and transmission functions, raw peak ratios among the three spectrometers differed by > 2. However, native software analysis on each instrument produced similar amounts of Cu to roughly \pm 5%. Note that sensitivity factors are more established for Cu 2p peaks than for Cu 3p peaks which may account for some variation. Naive transfer of data for analysis by non-native software was found to produce results significantly different than expected in some cases. This can be due to sensitivity factors or complications related to the instrument response function. These issues can be corrected but require care and verification or incorrect results will result.

AS-ThP-14 ToF-SIMS Characterization of Mechanocatalytically-Formed Carbonaceous Films on Nanocrystalline Pt_{0.9}Au_{0.1} Alloy: Insights into Chemistry, Structure, and Friction Behavior, Nicolas Molina, C. Edwards, The University of Texas at Austin; T. Babuska, J. Curry, F. DelRio, Sandia National Laboratories; J. Killgore, National Institute of Standards and Technology, Boulder; H. Lien, The University of Texas at Austin; M. Dugger, Sandia National Laboratories; F. Mangolini, The University of Texas at Austin

Nanocrystalline Pt-Au alloys have emerged as a highly promising class of hard and wear-resistant materials with potential application in several fields, including in electrical contacts (EC) and next-generation nanoelectromechanical systems (NEMS). While the mechanocatalytic formation of carbonaceous surface layers at the interface between sliding metallic contacts has been reported in the case of pure Pt (found to decrease adhesion and friction but increase the electrical resistance, resulting in reliability issues when Pt is used in NEMS switches), remarkably little is known about the chemistry, structure, and tunability of these interfacial layers in the case of Pt-Au alloys. In this study, we conducted tribological experiments on a nanocrystalline Pt_{0.9}Au_{0.1} alloy in the presence of ethanol (C₂H₆O) or isopropanol (C₃H₈O) vapor (partial pressure ranging from ultra-high vacuum (UHV) to 3 mbar). To gain insights into the chemical nature and structural properties of the mechanocatalytic, carbon-rich films formed on Pt_{0.9}Au_{0.1} surfaces, ex-situ time-of-flight secondary ion mass spectrometry (ToF-SIMS) depth profiling measurements were carried out. Notably, the development of a robust ToF-SIMS characterization methodology integrating molecular formula prediction (MFP) and multivariate statistical analysis (MVSA) allowed for highlighting subtle differences in elements' bonding configuration and functional moieties in the ultrathin carbon surface layers formed on Pt_{0.9}Au_{0.1} surfaces, including aromaticity of carbon atoms, hydrogenation, and molecular weight distribution. Our findings, demonstrating the intricate interplay between mechanocatalytic film formation, the nature of the organic gas environment, and gas pressure, not only advance our understanding of the tribological processes occurring on Pt-Au alloys, but also provide guidelines for tailoring the mechanocatalytic formation of carbonaceous surface layers

and modulating their tribological behavior by rationally varying the organic gas environments and pressure. SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.

AS-ThP-15 Quantification of Surface and Subsurface Structures of Complex Thin Films with LEIS, XPS and Sputter Depth Profile Simulations, Markus Valtiner, C. Bocanciu, J. Pichler, A. Celebi, TU Wien, Austria

Sputter depth profiling is an established technique to analyze surface and subsurface concentration profiles on various surfaces using different techniques such as XPS or AES. However, during sputtering both preferential sputtering as well as atomic intermixing do interfere with a detailed evaluation of surface and subsurface species. Here we show how a combination of Low Energy Ion Scattering and angle resolved XPS can reveal accurate depth distributions with high vertical profile resolution. Therefore, we also performed Monte Carlo based simulations of the sputtering processes, and fitted these to elemental distributions measured by LEIS and XPS during sputtering. We can show that our approach allows us to reconstruct accurate surface and subsurface distributions in complex materials and thin films including series of stainless steels, high entropy alloys as well as plasma etched silicon wafers with varying oxide thicknesses. Based on our approach a detailed elemental profiling with close to mono layer elemental distribution accuracy is possible. This is interesting for various fields including catalysis, corrosion as well semiconductor processing.

AS-ThP-16 Multimodal Characterization of Copper Hydroxy Chloride for Advanced Thermochemical Energy Storage Applications, Kavin Chakravarthy Thangaraj, X. Zhang, Washington State University, US; V. Prabakaran, V. Murugesan, A. Karakoti, Pacific Northwest National Laboratory

Developing efficient energy storage systems is paramount for achieving carbon neutrality and maximizing the use of renewable energy sources. Thermochemical energy storage systems (TCES), a distinct subclass of thermal energy storage systems (TES), have gained significant attention for their ability to store energy from intermittent energy sources like solar and wind. TCES work by storing and releasing thermal energy through processes such as adsorption, absorption, or chemical reactions. Salt hydrates are commonly studied for TCES applications due to their high energy density, cost-effectiveness, and eco-friendly qualities. However, challenges arise from the limited availability of suitable salt hydrates for specific uses and the need for additional materials like thermal conductive additives and phase stabilizers for optimal performance. Additionally, multimodal and in-situ characterization of TCES materials is required to identify the material degradation modes during energy storage and release cycles, which will enable the design of novel, better-performing materials.

To address these challenges, we explored the potential of copper hydroxy chloride (CHC), a double anion salt of copper, for TCES applications. The insolubility of CHC in water reduces deliquescence-associated performance degradation over extended cycling periods compared to other salt hydrate systems. Our study encompassed a multimodal evaluation of CHC for the application in TCES by analyzing its dehydration and hydration cycling behavior. Specifically, we utilized in-situ X-ray diffraction (XRD) and in-situ X-ray photoelectron spectroscopy (XPS) to discover a stagewise decomposition of CHC at different temperatures during its dehydration, resulting in the release of water and chlorine byproducts. By employing methods such as thermogravimetry- differential scanning calorimetry (TG-DSC), and a calorimeter paired with a humidity generator, we evaluated the temperature range suitable for hydration and dehydration of CHC, the associated heat changes (enthalpies) and the temperature range where the reversibility of reactions could be preserved. The multimodal and in-situ methods developed are largely applicable to other TCES materials for identifying the hydration, dehydration, and degradation mechanisms of salt hydrate-based materials and evaluating their promise as thermal energy storage systems, eventually contributing to the broader goal of sustainable and efficient energy storage.

AS-ThP-17 Observation of Multiple Flat Bands and Van-Hove Singularities in a Distorted Kagome System NdTi_3Bi_4 , Mazharul Islam Mondal, A. Sakhya, M. Sprague, University of Central Florida; B. Ortiz, Oak Ridge National Laboratory, USA; M. Matzelle, Northeastern University, US; N. Valadez, I. Bin Elius, University of Central Florida; B. Ghosh, A. Bansil, Northeastern University, US; M. Neupane, University of Central Florida

Kagome materials have attracted enormous research interest recently owing to their diverse topological phases and manifestation of electronic

correlation due to their inherent geometric frustration. Here, we report the electronic structure of a distorted Kagome metal NdTi_3Bi_4 using a combination of angle-resolved photoemission spectroscopy (ARPES) measurements and density functional theory (DFT) calculations. We discover the presence of two “flat” bands which are found to originate from the Kagome structure formed by Ti atoms with major contribution from Ti d_{xy} and Ti $d_{x^2-y^2}$ orbitals. We also observed multiple van Hove singularities (VHSs) in its electronic structure, with one VHS lying near the Fermi level (E_F). Our calculation indicates the presence of a bulk Dirac cone at the Γ point and a linear Dirac-like state at the K point with its Dirac node located very close to the E_F . Our findings reveal NdTi_3Bi_4 as a potential material to understand the interplay.

AS-ThP-18 Quantitative Analysis for Chromium Oxidation, Milton Vazquez-Lepe, University of Guadalajara, Mexico; A. Herrera-Gomez, O. Cortazar, CINVESTAV-Queretaro, Mexico; S. Aguirre, CIMAV-Monterrey, Mexico; C. Weiland, Brookhaven National Laboratory

The background in X-ray photoelectron spectroscopy, is formed from inelastic scattering. To evaluate oxide states for quantification, Tougaard background and Shirley background intensity must be assessed appropriately. The experimental background can be calculated with several methods with different contributions for the total area. For determination of composition, the Cr3s, Cr3p and O2s core levels were analyzed from 400 eV to 900 eV of emission source. These intensities were modified to evaluate the appropriate chemical quantification. Also, varying the photon energy applied, Shirley intensity is changing and was incorporated using the SVSC method that allows for accounting the differences for the assessment.

This research acknowledgment for the data obtained from National Synchrotron Light Source II of Brookhaven National Laboratory. This work is supported by the National Council of Humanities, Science and Technology by the Ciencia de Frontera under project 58518.

AS-ThP-19 Temperature Dependency of Doping Silicon with Phosphorus Using Ultra-Thin Films of P-Containing Minerals, Roman Konoplev-Esgenburg, P. Thissen, KIT, Germany

This work explores a novel approach using ultra-thin films of P-containing minerals which are Hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), Struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), and Monetite (CaHPO_4) and we expect high-temperature dependency of doping process due to different decomposition profiles. Thin films were prepared via a tethering by aggregation and growth method and subsequently processed by spike annealing. Minerals offer a large variety of materials that can be used in this doping process.

In-situ infrared (IR) spectroscopy reveals the decomposition of a mineral and its intermixing with the native silicon oxide at low temperatures (for Hydroxyapatite at 200°C). This process involves the migration of phosphate through the native oxide layer driven by a phase transformation into a more stable thermal oxide. Ultimately, the diffusion of phosphorus into the underlying oxide-free silicon layer is observed (for Hydroxyapatite at 700°C). By combining in-situ IR with electrical impedance spectroscopy (EIS) and X-ray photoelectron spectroscopy (XPS), the measurements allow us to conclude the following process. Firstly, the transport of phosphorus through the silicon oxide barrier and subsequent diffusion of phosphorus within the oxide-free silicon layer. Finally, the phosphorus concentration profile was confirmed by Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS).

To further explain and investigate experimental doping processes using thin films of P-containing minerals, mineral interfaces were modeled and DFT calculations were performed. The Nudged Elastic Bands (NEB) method provides us with the mechanism of phosphorus transport. Vibrational frequencies were calculated to correlate them with IR spectroscopy. Additionally, the DFT methods helped us optimize each corresponding doping process from the electrical perspective: electronic band structure, and pinned impurity levels that result in charge carrier trapping as each interface necessarily displays different electrical properties.

Surface Science

Room 120 - Session SS+AMS+AS+CA+LS-FrM

Advanced Surface Characterization Techniques & Mort Traum Presentation

Moderators: Donna Chen, University of South Carolina, Charles Sykes, Tufts University

8:15am **SS+AMS+AS+CA+LS-FrM-1 Infrared Spectroscopy as a Surface Science Technique**, *Michael Trenary*, University of Illinois - Chicago **INVITED**
Infrared spectroscopy is widely used to probe the vibrational properties of molecules in the gas, liquid, and solid phases. On the other hand, precise information on the structure and chemistry of solid surfaces, and of molecular adsorbates on solid surfaces, is best gained through use of surface science methods. These methods generally entail the use of single crystals, ultrahigh vacuum conditions, and surface sensitive techniques. Reflection absorption infrared spectroscopy (RAIRS) is a surface sensitive technique that can be used in ultrahigh vacuum to study molecular adsorption on well characterized metal single crystal samples. Unlike many other surface science methods, it can also be used under elevated gas pressures. The spectra obtained display features that are quite distinct from those of other phases of matter. For example, in the gas phase, rotational fine structure greatly complicates the appearance of the spectra but is absent in the spectra of adsorbed molecules. In the liquid phase, spectra are broadened by both static and dynamic effects often making it difficult to resolve vibrational peaks due to different chemical species. In polycrystalline molecular solids, molecules are randomly oriented relative to the electric field directions of the infrared radiation, limiting the value of the spectra as a structural probe. In contrast, when molecules adsorb on metal surfaces, they often adopt a definite orientation with respect to the surface normal. This orientation can be deduced through the surface dipole selection rule, which states that only normal modes with a component of the dynamic dipole moment oriented along the surface normal will be allowed. While IR spectroscopy in several forms has long been used to study molecular adsorption on supported transition metal catalysts, the high degree of heterogeneity of the catalyst surfaces leads to very broad peaks, with full width at half maxima (FWHM) of 10-50 cm^{-1} . In contrast, the FWHM of peaks measured with RAIRS on well-ordered metal surfaces can be quite narrow, in some cases even less than 1 cm^{-1} . When a polyatomic molecule exhibits sharp peaks throughout the mid-IR range, the advantages of performing RAIRS with a Fourier transform infrared spectrometer are most pronounced. This talk will cover the speaker's forty years of research using the technique of RAIRS to study molecular adsorbates on metal surfaces.

8:45am **SS+AMS+AS+CA+LS-FrM-3 Modeling Pipeline Surface Chemistry: Reaction of Monochloramine on Iron Surfaces**, *Kathryn Perrine, S. Pandey, O. Agbelusi*, Michigan Technological University

Monochloramine (NH_2Cl), a secondary disinfectant, is utilized to treat pathogens in the municipal water system, producing fewer halogenated disinfection by-products and lasting longer than free chlorine (hypochlorite). Although a weaker oxidant, NH_2Cl has the potential to corrode the surface of pipeline materials resulting in the dissolution of unwanted species. Copper and lead pipelines have been shown to corrode in chloramine solutions, however on iron materials the surface chemistry is unexplored. Complex chemistry occurs on the surface of pipelines at solution/metal interfaces, thus providing catalytic sites for dissociation, decomposition, and degradation. Iron comprises distribution pipelines and also exists as oxides in soils in the natural environment. Redox reactions occur on the surface of iron materials, thus initiating surface corrosion. Here, various active sites on iron are produced and known for high reactivity with nitrogen compounds. Our group employs a surface science approach to uncovering mechanisms at complex interfaces.

In this study, the reaction of monochloramine (NH_2Cl) was investigated on single crystal Fe(111) in ultra-high vacuum at the gas/solid interface using *in situ* infrared reflection absorption spectroscopy and Auger electron spectroscopy. At -160 °C, NH_2Cl molecularly adsorbs to the surface while the annealing leads to the loss of key vibrational modes, suggesting that either molecular desorption or dissociation occurs. These observations are contrasted with our findings at the solution/iron interface, where polarized modulated infrared reflection absorption spectroscopy (PM-IRRAS), ATR-FTIR, XPS, and XRD were used to assess the various regions after corrosion and their film growth. In solution, localized heterogeneous corrosion

products were observed and identified, suggesting different reaction pathways exist in strongly oxidizing solutions. These findings are important for understanding the mechanism of chloramines and water disinfectants on iron interfaces relevant for water quality, material degradation, and other complex environmental processes.

9:00am **SS+AMS+AS+CA+LS-FrM-4 Development of Tip-Enhanced Raman Spectroscopy for Solid-Liquid Interfaces**, *Naihao Chiang*, University of Houston

Tip-enhanced Raman spectroscopy (TERS) combines the spatial resolution of scanning probe microscopy (SPM) with the chemical sensitivity of Raman spectroscopy. TERS with sub-nanometer resolution has been demonstrated under ultrahigh vacuum conditions. We aim to extend this unprecedented chemical mapping capability to interfacial studies under the solution phase. Specifically, we have developed a scanning ion-conductance microscope for TERS (SICM-TERS) capable of interrogating soft samples. In this presentation, the instrumental design will be discussed first. SICM-TERS probe fabrication and evaluation will be followed. Then, a distance-dependent SICM-TERS measurement on two-dimensional MoS_2 sheets will be used to assess the strain created by the SICM probe in close proximity. Our results demonstrate the potential of combining TERS with SICM for obtaining chemical information at interfaces, thus setting the stage for future investigation into soft materials in electrolytic environments.

9:15am **SS+AMS+AS+CA+LS-FrM-5 Ion Based Pump-Probe: Probing the Dynamics Following an Ion Impact**, *Lars Breuer, L. Kalkhoff, A. Meyer, N. Junker, L. Lasnik*, Universität Duisburg-Essen, Germany; *Y. Yao, A. Schleife*, University of Illinois at Urbana Champaign; *K. Sokolowski-Tinten, A. Wucher, M. Schleberger*, Universität Duisburg-Essen, Germany

The study of ion-surface interactions is crucial for understanding material properties and their atomic-level dynamic responses. The transient nature of these interactions, occurring on ultrafast time scales, has so far limited direct experimental observation and has left the field reliant on computer simulations. Existing experimental methods, such as pump-probe techniques, have faced challenges in generating and precisely timing short, monoenergetic ion pulses essential for capturing these ultrafast phenomena.

Our group has pioneered a novel approach that overcomes these limitations by generating the world's shortest monoenergetic ion pulses in the keV regime, with a current duration of approximately 5 ps. These pulses are produced using femtosecond photoionization of a geometrically cooled gas jet, coupled with miniaturization of the ionization section.

In our experiments, we conduct ion-based pump-probe experiments observing the emission of hot electrons post-ion impact, similar to processes studied in two-photon photoemission (2PPE) experiments. Our findings not only demonstrate the feasibility of our approach and provide direct measurements of the ion pulse characteristics but also offer insights into the non-equilibrium dynamics of electronic excitation in solids following an ion impact. We can track the electronic excitation and determine the temporal evolution of a pseudo electron temperature.

This research opens new avenues for understanding the fundamental processes underlying ion-solid interactions, with significant implications for semiconductor manufacturing and materials science. Our work sets a new standard for temporal resolution in the study of ion-induced phenomena and lays the groundwork for future innovations in the field.

9:30am **SS+AMS+AS+CA+LS-FrM-6 How Hot Plasmonic Heating Can Be: Phase Transition and Melting of P25 TiO_2 from Plasmonic Heating of Au Nanoparticles**, *W. Lu, R. Kayastha, B. Birmingham, B. Zechmann, Zhenrong Zhang*, Baylor University

Plasmonic heating has been utilized in many applications including photocatalysis, photothermal therapy, and photocuring. However, how high the temperature can be reached for the surrounding media due to the collective heating of the plasmonic nanoparticles (NPs) and the impact of the heat dissipation on the surrounding media is not clear. Herein we studied the impact of plasmonic heat generated by resonantly excited gold (Au) NPs on P25 TiO_2 nanoparticle film. Under 532 nm continuous laser irradiation at the surface of the Au- TiO_2 , the surface evaporation of Au nanoparticles and phase transition of TiO_2 were observed at moderate laser power. More importantly, as high as the melting point of TiO_2 of 1830°C is confirmed from the molten TiO_2 rutile phase. When Au/ TiO_2 was irradiated with an off-resonance laser at 638 nm, no phase transformation or melting of TiO_2 was observed. The temperature calculation shows that the heating generated by Au nanoparticles is not localized. The collective heating from an ensemble of Au nanoparticles in the irradiated area produces a global

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temperature rise that melts TiO₂. Our results suggest that the photothermal effect could be a major mechanism in the plasmon-assisted photocatalytic reactions. The experimental observation of the high temperature of the supporting media suggests new applications for utilizing plasmonic heating, for example, additive manufacturing.

9:45am **SS+AMS+AS+CA+LS-FrM-7 Kinetics and Dynamics of Recombinative Desorption of Oxygen from Silver and Rhodium Surfaces, Dan Killelea**, Loyola University Chicago

The ability to obtain velocity distributions of molecules desorbing from surfaces with both high temporal precision and angular resolution provide newfound insight into both the kinetics and the dynamics of recombinative desorption and subsurface emergence.

I will discuss our observations of subsurface oxygen emerging from beneath Rh(111) and how the velocity distribution shifts in comparison to the thermally-dominated desorption pathways found for surface-adsorbed oxygen. In addition, it was recently discovered that decomposition of oxygenaceous surface phases on Ag(111) also exhibit pronounced shifts in the energetics of the desorbing oxygen molecules. I will discuss these observations and their potential impacts in oxidation reactions in heterogeneously catalyzed reactions over transition metal surfaces.

10:00am **SS+AMS+AS+CA+LS-FrM-8 Mort Trau Award Announcement**,

10:30am **SS+AMS+AS+CA+LS-FrM-10 Unveiling Surface Mysteries with XPS Lab from Scienta Omicron, Tamara Sloboda**, Scienta Omicron, Sweden; *P. Amann*, Scienta Omicron, Germany; *B. Gerace, F. Henn, A. Yost, X. Zhang*, Scienta Omicron; *M. Lundwall*, Scienta Omicron, Sweden

Surface analysis is paramount for understanding material properties, and Scienta Omicron's XPS Lab system excels in this realm. Featuring a compression unit for superior count rates and sensitivity, it offers unparalleled quantitative XPS enabled by a true counting multi-anode detector inside the Argus CU analyser. This unique detector employs 128 individual counters connected to a striped-anode array. With a linear response extending to the highest count rates and an exceptional dynamic range, it ensures high resolution precise measurements across various sample types.

The versatility of XPS Lab is evident through its scanning, imaging, snapshot, and dynamic measurement modes (see Figure 1), enabling researchers to tailor their experiments to specific needs. The chemical state mapping capability of the XPS Lab provides comprehensive insights into surface chemistry, empowering researchers to unravel complex phenomena.

Illustrating its prowess, case studies span catalysis, energy storage, semiconductor technology, and biomaterials, showcasing its ability to address diverse research challenges. Recent enhancements further strengthen its capabilities, solidifying XPS Lab as the premier choice for XPS analysis.

In summary, Scienta Omicron's XPS Lab system offers unmatched precision, sensitivity, and versatility, driving advancements in surface science and materials research.

10:45am **SS+AMS+AS+CA+LS-FrM-11 Investigation of Stannane (SnH₄) Decomposition and Sticking Coefficient on Varied Metal Surfaces in EUV Lithography Environments, Emily Greene, N. Barlett, D. Qerimi, D. Ruzic**, University of Illinois at Urbana-Champaign

In the context of extreme ultraviolet (EUV) lithography, the evaporation of tin droplets frequently leads to the deposition of tin on various chamber surfaces, including collector mirrors. A prevalent method to remove this tin deposition involves hydrogen plasma etching, which transforms the deposited tin into stannane (SnH₄). This compound, existing in a gaseous state under operational conditions, can be evacuated from the chamber using a vacuum pump. However, stannane is characterized by its instability, tending to decompose and adhere to various surfaces within the chamber.

To systematically study the decomposition behavior of stannane, a specialized experimental chamber has been designed. This chamber integrates a load-lock mechanism for inserting a test tube containing liquid stannane into a loading section, which is isolated from the main vacuum chamber by a valve. Within the main chamber, a quartz crystal microbalance (QCM), regulated by a cartridge heater, measures the mass of stannane deposits. The QCM will be set to temperatures between 30-300 °C. Upon opening the valve, the stannane vaporizes and interacts with the temperature-controlled QCM, facilitating the quantitative

determination of the sticking coefficient as a function of both the surface material and the temperature.

Stannane is synthesized through the reaction of LiAlH₄, SnCl₄, C₈H₁₈O, and C₄H₁₀O₂. The four chemicals are mixed in a 3-neck flask while under vacuum. The reaction produces SnH₄ which flows through three U-tubes traps. The first trap is held at -96 °C to trap precursors, the second two traps are held at -196 °C and trap the stannane. The stannane is increasingly pure the more traps are used.

This investigation aims to understand and quantify the mechanisms of stannane deposition and decomposition, enhancing the maintenance and efficiency of EUV lithographic systems by optimizing the cleaning protocols for tin contamination.

11:00am **SS+AMS+AS+CA+LS-FrM-12 First Principles Methods for Predicting Surface Reaction Mechanisms for Chemical Functionalization of Semiconductor Surfaces, Roberto Longo, S. Sridhar, P. Ventzek**, Tokyo Electron America Inc.,

The density of semiconductor devices continues to increase, accompanied by the subsequent scaling down of the critical dimension (CD) size, which is now on the order of a few nanometers. This results in device structure changes, from two-dimensional (2D) to three-dimensional (3D) structures, because the CD size has reached its limit of reduction. To accomplish this, precise chemical modification of the required surfaces with atomic scale precision is key to obtain the desired geometric control. Precise modification implies being able to leverage knowledge of individual plasma born species and surface interactions. Unfortunately, species specific chemical interaction mechanisms in the context of reactive ions and chemical etching are still poorly understood for the full range of chemical environments at play. Once dissociated in plasma radicals, there might be a wide array of compositions. For similar atomic compositions, variations in the molecular structure of the chemical precursor can also result in significant differences as to the surface modifications and subsequent etching characteristics. The chemical nature of the surface including coverage and chemical activity add significant dimensionality to the problem of controlling plasma surface interactions in general. We divide the problem of elucidating plasma surface interactions into two major categories for practical purposes: hydrofluorocarbon driven for oxide etch and halogen driven for silicon etch. We present here semiconductor surface modeling with general characteristics and investigate the reaction mechanisms undergone by a large variety of hydrofluorocarbon molecular precursors using density-functional theory (DFT), with a focus on reactive halogen adsorption. Given the large parameter space of this problem, we describe computational approaches that efficiently and accurately generate fundamental data. Physical and chemical surface reactions and the corresponding byproducts are identified, obtaining self-limitation thresholds for each specific functionalizing chemistry. Therefore, our computational results provide valuable insights on the complex physical, chemical, and dynamic molecular and ion interactions with functionalized semiconductor surfaces, paving the road for designing tailored strategies with the desired outcome for each specific system.

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