Monday Morning, September 22, 2025

Applied Surface Science
Room 209 B W - Session AS+BI+CA-MoM

The Power of SIMS

Moderators: Alexander Shard, National Physical Laboratory, **Tanguy Terlier**, Rice University

8:45am **AS+BI+CA-MoM-3 Inspection of Next Generation EUV Resists with NP-SIMS**, ***Markus Langner***, *Gregrey Swieca,* California State University Northridge*; Won-Il Lee, Shixian Ha,* Stony Brook University/Brookhaven National Laboratory*; Nikhil Tiwale, Chang-Yong Nam,* Brookhaven National Laboratory*; Michael Eller,* California State University Northridge

The rapid advancements of the semiconductor industry demand constant innovations at every step of the microchip manufacturing process. Due to the recent jump towards extreme ultraviolet lithography (EUVL), novel approaches to photoresists are necessary, since conventional chemically amplified resists (CARs) exhibit poor EUV sensitivity and the photon density of EUV light sources is orders of magnitude lower compared to deep ultraviolet (DUV) sources. As a result of low photon density, the nature of EUVL is more stochastic, which leads to challenges in the photoresist chemistry to yield good critical dimension uniformity (CDU) and line edge roughness (LER). Hybrid resists of an organic polymer infiltrated with an inorganic metal solve the low EUV sensitivity problem while exhibiting improved etch resistance. However, it is necessary to ensure high homogeneity of the infiltration process, since the size of the infiltrated molecular moieties is comparable to the desired critical dimensions. Analytical techniques are often unable to yield analysis of the organic and inorganic components of a sample at the same time, in conjunction with high lateral resolution and can as a result not resolve inhomogeneity in the resist at a necessary spatial scale. Nano-projectile secondary ion mass spectrometry (NP-SIMS) is a mass spectrometry technique involving the stochastic bombardment of the sample using nano-projectiles separated in time and space, instead of a continuous ion beam. Each impact yields an individual mass spectrum resulting from an impact crater with 10-15nm in diameter, which allows statistical analysis of the sample and emitted secondary ions from different impacts and thus different locations. In this work we studied samples of polymethylmethacrylate (PMMA) infiltrated with InOx via vapor-phase infiltration (VPI) and investigated the uniformity of the infiltration process utilizing NP-SIMS experiments. The data suggests that one cycle of VPI yields an inhomogeneous distribution of In in PMMA, which improves with further infiltration cycles. The abundance of In species increases linearly with the number of cycles as well, indicating successful infiltration for each cycle up to four. Cluster species such as In2+, In2O+ display a non-linear increase with infiltration cycles, which leads to the hypothesis, that the amount if infiltrated indium is as desired but it aggregates in small clusters, which could affect pattern performance of the resist. This research is supported by the U.S. Department of Energy Office of Science Accelerate Initiative Award 2023-BNL-NC033-Fund.

9:00am **AS+BI+CA-MoM-4 Diffusion Study of Sodium in Hard Carbon Anode Active Materials Using a Novel in Situ ToF-SIMS Approach**, ***Pascal Dippell***, *David Schaefer, Lysander Q. Wagner, Alexander Weiß, Bernd Smarsly, Marcus Rohnke,* Justus Liebig University Giessen, Germany

The incorporation, transport and storage of Na in hard carbon (HC) anodes play a crucial role in modern sodium-ion batteries (SIBs) and affect their electrochemical performance.Until now,the diffusion mechanism of Na in the HC microstructure hasnot been fully understood.The most prominent model, whichisdiscussed in the literature,is the adsorption-intercalation-filling model, which includes diffusion along an interface of a pore and through the bulk of the HC. Most diffusion studies use electrochemical methods, but their evaluation is limited by overlapping processes in the cell, which prevents a complete understanding of sodium diffusion.[1]

In this work, we developeda new in situ ToF-SIMS approachforthe determination of the microscopic Na diffusion processes in HC. Therefore,we chose a well-defined HC thin film with an ultra-pure Na layeron top as model system, to obtain a precise interface between the twocomponents. For the preparation of theHC|Na model system we connected anNa effusion cell to an ultra-high vacuum (UHV) preparation chamber, which is directly attached to theToF-SIMS analysis chamber. Thisexperimental setup enables a defined preparation ofour HC|Nainterface and,moreover, allows an accurate determination of the diffusion parameters.After a definedtime, theNa diffusioninto HC is stopped by cooling downthe system to −130°C, and the diffusion profiles are preserved.

By SIMS depth profiling, we received complex diffusion profiles thatinclude several transport parameters.The SIMS crater analysis was possible through the use of an implemented SPM. As a result of these depth profiles and additionalfinite element calculations, a separation of the different transport processesbecamepossible.Specifically, we observed coupled Na bulk diffusion, which is a solid-statetransport process, and Na pore diffusion, which occurs along an interface.The proposed diffusion model is complemented by additional experiments, which displayed the structural behavior of the HC thin films. These experiments include infiltration studies with liquid electrolytes and a tracer ion for demonstrating the accessibility of the pore system, as well as high resolution electron microscopy for imaging the structure of the HC.

References

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9:15am **AS+BI+CA-MoM-5 Investigating Ionic Motion in Memristors via Topographically Corrected ToF-SIMS**, ***Jacob Shusterman***, Oak Ridge National Laboratory, USA

Secondary ion mass spectrometry (SIMS) is a powerful analytical technique which combines the benefits of high-resolution mass spectrometry with sub-micrometer lateral resolution to identify the spatial distribution of elements and molecules in a sample. Capable of both two- and three-dimensional (3D) analysis, SIMS enables chemical imaging of surfaces, devices, and bulk materials, proving a valuable tool for material characterization. Recent studies have successfully demonstrated applications of SIMS for the investigation of ionic motion in resistively switchable neuromorphic materials such as memristors. However, interpreting SIMS data, especially for microelectronic and nanoscale devices, can be difficult due to significant surface topography and data complexity. This makes it challenging to draw accurate conclusions regarding material composition or chemical changes (e.g. ionic motion) without addressing these features in native 3D SIMS chemical images. Here, we discuss various methods for topographical correction and reconstruction of SIMS data to study ionic mobility in memristive thin films.

Two prominent categories of data correction methods are considered including purely mathematical based post-processing techniques and multimodal approaches combining SIMS with atomic force microscopy. These methods are further applied to TaO_x/Ta memristors to reveal ionic migration associated with resistive switching. Here, lower switching currents (< 10µA) revealed oxygen ion migration and preserved memristic behavior of the thin film device. Conversely, resistive switching with currents greater than 10 µA revealed titanium ion migration from the bottom electrode resulting in irreversible switching to a high conductive state. This research can help gain knowledge of fundamental phenomena associated with memristive behavior of materials for implementation in new generations of microelectronic devices.

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.

9:30am **AS+BI+CA-MoM-6 Standardless, Semi-quantitative ToF-SIMS using the Full Spectrum Method (FSM)**, ***Nicolas Molina Vergara***, *Camille Edwards, Andrei Dolocan, Filippo Mangolini,* University of Texas at Austin

The accurate quantification of the hydrogen content in materials remains a significant analytical challenge despite its critical importance in determining material performance, stability, and functionality across numerous applications. Currently, only a limited number of techniques—such as hydrogen forward scattering (HFS) and nuclear reaction analysis (NRA)—provide accurate hydrogen quantification measurements, typically achieving relative errors between 3% and 10%. While time-of-flight secondary ion mass spectrometry (ToF-SIMS) offers excellent chemical characterization capabilities, its application for hydrogen quantification has been primarily qualitative due to matrix effect complications and the absence of appropriate relative sensitivity factors. Here, we report the first successful application of the Full Spectrum Method (FSM) for quantitative hydrogen analysis in organic polymers. Despite being documented in fewer than six publications over the past two decades, FSM represents a

promising approach for semi-quantitative ToF-SIMS analysis by exploiting large ion clusters that incorporate numerous neutral atoms, effectively mitigating matrix effects as cluster size increases. We systematically quantified hydrogen content in a series of polymers—polypropylene (C_3H_6), polystyrene (C_8H_8), polyethylene terephthalate ($C_{10}H_8O_4$), and polytetrafluoroethylene (C_2F_4)—achieving a high degree of agreement with their nominal hydrogen composition and further verified by complementary measurements performed on identical samples using reflection electron energy loss spectroscopy (REELS). Our results establish a pathway for standardless, semi-quantitative ToF-SIMS analysis without requiring complementary analytical techniques, significantly enhancing the practical utility of ToF-SIMS instrumentation.

9:45am **AS+BI+CA-MoM-7 AVS Medard Welch Award Talk: High Resolution Molecular Imaging by Mass Spectrometry – The OrbiSIMS Odyssey**, ***Ian Gilmore***, National Physical Laboratory, U.K. **INVITED**

Nuclear magnetic resonance and high-performance liquid chromatography mass spectrometry are the "gold standards" for molecular identification. However, they have limited spatial information. Conversely, techniques with high spatial resolution such as electron microscopy, have low molecular identification information. Generally, from an analytical perspective, this creates what can be termed the "Molecular Uncertainty Principle", where the more certain we are about a molecule's identity, the less certain we are about its localization [1]. This is a frustrating limit for measurements at the frontiers.

In 2017, NPL introduced the OrbiSIMS technology [2] with an objective to simultaneously provide molecular identification and localisation as close to this limit as possible. Since then, the number of OrbiSIMS instruments around the world has increased significantly and the community [https://www.npl.co.uk/mass-spectrometry/orbisims/resources] of users and range of applications has grown. Here we recount the OrbiSIMS odyssey from the original concept to the latest advances in cryo-OrbiSIMS [3,4], illustrated with examples of the applications in advanced materials [5] and life-sciences [6]. In a look to the future, the concept for a quantum detector to boost Orbitrap sensitivity by an order of magnitude will be presented [7].

References

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[5] G F Trindade et al., Direct identification of interfacial degradation in blue OLEDs using nanoscale chemical depth profiling. Nature Communications, 2023. 14 (1): p. 8066.

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10:30am **AS+BI+CA-MoM-10 ASSD Peter Sherwood Award Talk**, ***David Scurr***[1], University of Nottingham, UK **INVITED**

11:00am **AS+BI+CA-MoM-12 Delineating Spatial Cellular Complexities Using Multi-omics Approach by GCIB-SIMS**, ***Hua Tian***, University of Pittsburgh **INVITED**

The molecular and cellular microenvironment plays a critical role in determining biological function, multicellular organization, and cell fate. However, delineating multilevel biomolecular interactions within the same tissue or cells remains challenging due to limitations in analytical approaches and sample preparation compatibility.

To address this, we present a multimodal SIMS approach incorporating water cluster ion/C_{60} beams and a cryogenic workflow, enabling untargeted lipidomics/metabolomics imaging (in both positive and negative modes) and targeted proteomics in near-native-state tissue at 1 μm spatial resolution. Combined with neuron-linked computational analysis, this method reveals the biomolecular networks and metabolic states of distinct cell types.

To demonstrate the power of this approach, we imaged liver and skin tissues, integrating metabolites, lipids, and proteins within the same cells to visualize cell-type-specific metabolic variations. Our workflow captures >200 key ions (e.g., lipids and essential metabolites) and identifies diverse cell types (e.g., stem cells, lymphatic cells, immune cells, and senescent cells) in regions such as the liver portal/central vein and hair follicles.

Further computational integration aligns multiomics data with segmented cells for clustering analysis, uncovering metabolic and cellular gradients in the liver and the stem cell microenvironment of hair follicles during aging. This study establishes cryogenic Dual-SIMS as a powerful tool for single-cell multiomics imaging, revealing that metabolic and cellular organization is crucial for tissue and stem cell function.

11:30am **AS+BI+CA-MoM-14 Arsenic Quantification in SiGe: Advancing Accuracy with Orbitrap™-SIMS**, ***Alexis Franquet***, IMEC Belgium; *Alexander Pirkl*, IONTOF GmbH, Germany; *Rita Tilmann*, IMEC Belgium

For over 50 years, Secondary Ion Mass Spectrometry (SIMS) has been crucial in the microelectronic industry providing precise analysis of dopants and impurities in semiconductors [1]. Initially used for blanket samples, SIMS now must analyze patterned samples due to the shift from 2D to 3D devices to continue to support effective process development and optimization in the Fab. This shift presents challenges, including measuring features smaller than the beam spot size and dealing with complex mass spectra with more and more mass interferences due to increased number of elements present in the devices. As a result, SIMS analysis has become increasingly complex, making it harder to extract precise information about bulk and layer composition, dopant quantification and layer uniformity. To meet this need of ultimate lateral resolution without scarifying sensitivity, innovative approaches like Self-Focusing SIMS (SF-SIMS) have been developed, allowing SIMS to profile dopants and quantify bulk composition of multilayers stacks in very small structures [2]. This advancement is particularly crucial for modern devices that incorporate materials such as SiGe doped with As. However, measuring As in SiGe remains a significant challenge due to strong mass interference between As and GeH signals at mass 75 [3]. This challenge is even more pronounced for low-dose As implantation in small SiGe structures, where conventional SIMS instruments lack the mass resolution required for accurate quantification. In this study, we leverage the cutting-edge Orbitrap mass analyzer in the M6 Hybrid instrument to overcome these limitations. The Orbitrap enables mass resolution of more than 240000, which allows to suppress the mass interference at mass 75. We will assess the ability of the Orbitrap to accurately quantify As in SiGe samples, comparing its detection limits, dynamic range, and overall performance against other mass analyzers, including Time-of-Flight, Magnetic Sector, and Quadrupole systems. We will show how the use of calibration curves for both As and Ge quantification for As:SiGe ranging from 0 to 100 Ge at.%, allows to apply SF-SIMS (in Orbitrap) to quantify accurately As:SiGe lines of less than 20nm wide.

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[1] **ASSD Peter Sherwood Award**

Applied Surface Science
Room 209 B W - Session AS-MoA

Quantitative Surface Analysis I

Moderators: David Morgan, Cardiff University, **Lyndi Strange**, Pacific Northwest National Laboratory

1:30pm **AS-MoA-1 Quantified Photoemission Using Ga Kα (9.25 keV) Hard X-Rays Applied to Advanced Materials***, **Ben Spencer**, Abdulrhman Alsaedi, Liam Dwyer,* The University of Manchester, UK*; Benjamen Reed, David Cant, Alexander Shard,* National Physical Laboratory, U.K.*; Michael Baker, Alex Walton, Nicholas Lockyer, Wendy Flavell,* The University of Manchester, UK **INVITED**

X-ray photoemission spectroscopy (XPS) sampling through the sub-surface towards the bulk requires higher X-ray photon energies generating higher Kinetic Energy photoelectrons. We detail how this is enabled in the Scienta Omicron Hard X-ray Photoelectron Spectrometer (HAXPES) laboratory instrument utilising a 9.25 keV X-ray source (Ga Kα MetalJet, Excillum) and EW4000 electron energy analyser [1-6]. Laboratory systems offer some important advantages over synchrotron X-ray sources including easier access, highly reliable source intensities, and the development of reliable quantification methodologies [7]. We demonstrate how HAXPES can extract information significantly further into the surface compared to traditional approaches, with sampling depths up to twenty times the inelastic mean free path enabled by analysis of the inelastic background [2,5], and we detail the metrology developed to ensure accurate quantification across the measurable Binding Energy range [2-6]. 9.25 keV HAXPES enables measurement of higher Binding Energy core levels, such as 1s core levels of first row transition metals (up to Cu 1s at 8.98 keV), and previously unmeasured Auger transitions. We highlight measurements of higher Binding Energy core levels for quantification and chemical state identification applied to energy materials, where deeper core levels offer enhanced relative sensitivities compared to traditional XPS [8], and including the analysis of satellite peak structures as compared to theoretical calculations. As such we demonstrate the capabilities of laboratory HAXPES with a view to future developments and applications to advanced materials research.

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2:00pm **AS-MoA-3 Quantification of Bulk MoS_2 and Characterization of Mo Oxides by Cr Ka-excited HAXPES : Issues and Tentative Improvements***, **Olivier Renault**, Nicolas Gauthier, Mario Ghostine, Roman Charvier,* CEA-Leti, France*; Bruno Domenichini,* Université Bourgogne-France Comté, France

In this presentation, we will present HAXPES results related to Mo compounds of practical interest in device technology. Spectra of bulk MoS2 were acquired with a Cr Ka source following a careful measurement protocol [1]. The latter includes checking for instrument stability, use of pure-element relative sensitivity factors and an improved determination of the spectrometer transmission function. The results indicate large errors in the determination of the stoechiometry depending on the selected core-lines. Preliminary results obtained on pure metallic, homogeneous Mo surfaces show potential improvements if the measured intensity takes into account inelastic losses which are important at high kinetic energies. A second part will be dedicated to sub-stoechiometric Mo oxide films with a particular attention to beam effects, the impact on the determination of the stoechiometry along with suitable protocols for accessing deeply buried interfaces.

In a second topic, we will address the case of sub-stoechiometric Mo oxide films which are photochromic materials and are prone to alterations upon X-ray irradiation, with consequences on the detrmination of the Mo/S ratio. We will comment on the origins of these altaerations and propose solutions towards a reliable analysis, before presenting results regarding deeply buried interfaces.

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Acknowledgment : This work, carried out on the Platform for Nanocharacterisation (PFNC), was supported by the “Recherche Technologique de Base” and "France 2030 - ANR-22-PEEL-0014" programs of the French National Research Agency (ANR).

2:15pm **AS-MoA-4 Routine, Integrated Ag-Lα Haxpes – Acquisition and Quantification***, **Miroslav Michlicek**,* Thermo Fisher Scientific, CZ, Czechia*; Keith McCourt, Paul Mack,* Thermo Fisher Scientific, UK

Hard X-ray photoelectron spectroscopy (HAXPES) has significantly evolved since its inception and early use in synchrotron facilities, and is nowadays readily available in lab-based instruments. Especially when used in tandem with standard Al-Kα XPS spectroscopy, the method offers deep insight into the electronic structure of materials and can help to resolve some ambiguities inherentto standard XPS. Despite its advantages, HAXPES has faced several challenges, including accurate peak quantification.

This work addresses the steps necessary to overcome these quantification challenges for Ag-Lα HAXPES data. We first discuss critical experimental considerations for ensuring accurate and reproducible measurements, namely the reproducibility of the monochromator crystal. We then examine the three pillars supporting the peak area quantification: relative sensitivity factors, escape depth correction and instrument transmission function. In particular, we detail our approach to estimating the instrument transmission function. The robust, factory-default estimate was acquired by global fitting of noble metals (Au, Ag, Cu) spectral datasets collected from multiple instruments. Finally, we present the combined quantification accuracy on several pure elements (ie. from different transitions) and binary compounds with an expected stoichiometry. In conclusion, the integrated automated anode switching coupled with data quantification software, represents a significant step forward in making routine Ag-Lα HAXPES acquisition practical and reliable.

2:30pm **AS-MoA-5 Non-Destructive Depth Profiling by Variable Energy PARXPS (VE-PARXPS)***, **Paul Dietrich**, Francesca Mirabella, Martin Breitschaft, Andreas Thißen,* SPECS Surface Nano Analysis GmbH, Germany

Chemical analysis of contemporary materials frequently entails the characterization of surface and bulk compositions. EnviroMETROS LAB and FAB provide a monochromated small spot X-ray source with up to three different photon energies giving different surface and bulk sensitivities due to the variation in kinetic energy of the emitted photoelectrons. Moreover, the angle-resolving, wide-angle electron analyzer AEOLOS 150 AD-CMOS together with the software enables high sensitivity and high resolution analysis with direct non-destructive depth profiling.

Variable Energy X-ray photoelectron spectroscopy (VE–XPS) employs tunable X-ray sources, such as synchrotrons or laboratory-based monochromators, to adjust the photon energy. This adjustment enables depth profiling and enhanced sensitivity to different core-levels. By tuning the photon energy, the kinetic energy of emitted photoelectrons can be controlled, effectively changing the inelastic mean free path (IMFP). This capability allows for analysis of surface, subsurface, and bulk regions.

In parallel angle-resolved XPS (PARXPS) photoelectrons at various emission angles are collected simultaneously using a wide-angle analyzer. This method facilitates the concurrent acquisition of spectra from multiple angles, thereby enhancing the efficacy and precision of probing depth and electronic structure. PARXPS allows to create concentrational depth profiles from data that was taken for different photoelectron emission angles. A parallel spectra collection of individual angle channels is possible with the AEOLOS 150 AD-CMOS analyzer, developed especially for performing PARXPS measurements.

VE-XPS allows for the adjustment of probing and information depth, while PARXPS provides angular-resolved data, enabling non-destructive depth profiling with enhanced accuracy. By varying the energy and emission angle, more detailed information can be extracted, which is crucial for materials such as layer stacks and semiconductors. The combination of tunable energy with angular resolution enables the differentiation between surface, interface, and bulk states, thereby facilitating the acquisition of comprehensive structural information. The capacity to adjust depth sensitivity minimizes the occurrence of misinterpretation arising from charging effects or contributions from deeper layers, ensuring the reliability and precision of the measurement process. The combination of VE-XPS and PARXPS, allows to obtain a much richer dataset, enabling a more precise and comprehensive understanding of material surfaces and interfaces

2:45pm **AS-MoA-6 Efficient, Non-Destructive Characterization of Buried Layer Chemistry - Introducing the Next-Generation High-Intensity Deep HAXPES Instrument**, ***Marcus Lundwall**, Tamara Sloboda, Dick Allansson,* Scienta Omicron, Sweden*; Daniel Beaton,* Scienta Omicron*; Susanna Eriksson,* Scienta Omicron, Sweden

Buried interfaces in electronic devices—such as batteries, solar cells, and transistors—play a critical role in device performance. Reliable instrumentation for characterizing these interfaces is therefore essential for material development. While X-ray photoelectron spectroscopy (XPS) is a powerful technique for probing chemical states at surfaces, it cannot directly access buried interfaces without sputtering or etching, which can introduce artifacts. Hard X-ray photoelectron spectroscopy (HAXPES) offers a solution by providing increased information depth, enabling non-destructive characterization of layered structures. As a result, HAXPES has become an invaluable tool in materials research, particularly for applications involving semiconductor thin films, polymer materials, metal surfaces, and coatings.

This presentation will provide an overview of HAXPES applications, with a focus on non-destructive studies of buried interfaces in electronic devices, operando studies and oxidation processes. Additionally, we will introduce recent advancements in lab-based HAXPES systems. The latest generation features a Ga Kα 9.25 keV MetalJet microfocus HAXPES X-ray source, alongside improvements in electron detection efficiency. Compared to its predecessor, the new system offers a several-fold increase in acquisition speed while maintaining a proven probing depth of up to 50 nm. To fully leverage these enhancements, the sample handling and navigation system has been upgraded with a larger mounting area, enabling automated acquisition across a higher number of samples and measurement points. These innovations make high-end, high-energy Deep HAXPES a viable high-throughput technique beyond synchrotron facilities.

3:00pm **AS-MoA-7 Quantification of the Carbon Hybridization State via C 1s XPS: Possibilities and Limitations**, ***Filippo Mangolini**,* The University of Texas at Austin*; Michael Walter,* Fraunhofer Institute for Mechanics of Materials IWM, Germany*; J. Brandon McClimon, Robert W. Carpick,* University of Pennsylvania*; Michael Moseler,* Fraunhofer Institute for Mechanics of Materials IWM, Germany

The determination of the carbon hybridization state in carbon-based materials is of pivotal importance owing to the strong dependence of the physical, chemical, and mechanical properties of these materials on the carbon bonding configuration. Despite the relevance of published studies, the quantification of the hybridization state of carbon atoms by X-ray photoelectron spectroscopy (XPS) is still a surface-analytical problem owing to the challenges associated with the unambiguous identification of the characteristic binding energy values for sp^2- and sp^3-bonded carbon. Here, we performed density functional theory (DFT) calculations to determine the binding energy values of C 1s core electrons on the absolute energy scale for model structures of a class of carbon-based materials, namely amorphous carbon (a-C). In the case of hydrogen-free a-C, the DFT calculations indicate that the average C 1s binding energy for sp^3-bonded carbon atoms is approximately 1 eV higher than the average binding energy of sp^2-hybridized carbon atoms. Notably, the introduction of hydrogen in the a-C network reduces the distance between the characteristic signals of sp^3- and sp^2-bonded carbon due to the increased ability to screen the core hole by neighboring hydrogen atoms as compared to carbon atoms. These results, which are in qualitative agreement with experimental XPS spectra acquired on a-C materials containing different hydrogen content, highlight that the characterization of the carbon hybridization state on the basis of fitting C 1s XPS spectra with two synthetic components, one assigned to sp^2-bonded carbon and one assigned to sp^3-bonded carbon, is not physically accurate in the case of a-C specimens containing hydrogen. This work can assist surface scientists in the use of XPS for the accurate characterization of carbon-based material.

3:15pm **AS-MoA-8 Correlative XPS and EBSD with Cluster Ion Etching for Enhanced Surface Preparation**, ***Simon Bacon**, Helen Oppong-Mensah, Robin Simpson, Paul Mack, Tim Nunney,* Thermo Fisher Scientific, UK

Electron Backscatter Diffraction (EBSD) is a critical technique in materials science, providing detailed crystallographic information that is essential for understanding the microstructure and properties of materials. EBSD is widely used to analyse grain size, orientation, and phase identification, which are fundamental for optimising material properties and performance in various applications. The high spatial resolution and sensitivity of EBSD make it an invaluable tool for characterising such features in metals, ceramics, semiconductors, and other advanced materials.

However, the preparation of samples for EBSD presents several challenges. Surface contamination and damage can significantly affect the quality and accuracy of EBSD data. Traditional mechanical polishing methods often introduce surface artifacts that obscure the true microstructure of the sample. Ensuring the precise alignment and correlation of data between different analytical techniques also poses difficulties and can hinder any characterisation efforts.

To address these challenges, we demonstrate a solution that integrates a correlative XPS-SEM workflow (CISA) with cluster ion beam etch sample preparation. XPS offers detailed surface chemical analysis in the form of elemental composition and chemical state information. Cluster etching provides a controlled method for cleaning and defining surfaces, which helps to minimise contamination and damage. The CISA workflow ensures accurate alignment and correlation of data between XPS and EBSD analyses. By utilising specialised sample holders and advanced software alignment routines, we can achieve precise co-location of analytical data, which improves reliability and reproducibility of the results.

In summary, the combination of XPS and EBSD is a powerful one, offering comprehensive chemical and microstructural characteriation of materials. The use of both cluster ion beam etching as an integrated sample preparation method and the CISA workflow for precise feature location and alignment, ensures high quality, reliable cross-technique data to facilitate advancements in materials science and engineering.

3:30pm **AS-MoA-9 Enhanced Depth Profiling of Polymer Multi-Layer Samples Using Combined Femtosecond Laser Ablation and Cluster Ion Beams in XPS**, ***Robin Simpson**,* Thermo Fisher Scientific, UK*; Charlie Chandler, Mark Baker,* University of Surrey, UK*; Tim Nunney,* Thermo Fisher Scientific, UK

X-ray Photoelectron Spectroscopy (XPS) is a critical technique for surface and interface analysis, providing elemental and chemical state information. Depth profiling of polymer multi-layer samples, however, presents significant challenges due to the potential for sample damage and chemical modification during the sputtering process. To address these challenges, we propose a novel approach that integrates femtosecond laser ablation with cluster ion beam sputtering for XPS depth profiling.

Femtosecond laser ablation offers precise material removal with minimal thermal damage, making it ideal for initial bulk material removal. Cluster ion beams, known for their gentle sputtering capabilities, are then employed for fine-scale depth profiling, reducing the risk of chemical alteration and maintaining the integrity of the polymer layers.

In this study, we systematically investigate the combined use of femtosecond laser ablation and cluster ion beams on polymer multi-layer samples. We calibrate the laser and ion beam parameters to optimize ablation rates, minimize surface roughness, and ensure accurate depth resolution. Our results demonstrate significant improvements in depth profiling accuracy and chemical specificity, allowing for detailed characterization of each polymer layer.

The hybrid approach enhances the depth profiling capability of XPS, providing a powerful tool for analyzing complex polymer structures. The integration of femtosecond laser ablation and cluster ion beams enables high-resolution depth profiling, offering new insights into the composition and chemical states of multi-layer polymer samples.

Our findings highlight the potential of this combined technique to advance the field of polymer analysis and other applications requiring precise depth profiling. Future work will focus on further optimization of the parameters and extending the technique to a wider range of materials.

4:00pm **AS-MoA-11 Contribution of Imaging X-Ray Photoelectron Spectroscopy (Xps) to Characterize Spatial Chemical Distribution of Zno Nanoparticles in a Protective Sio2 Matrix for Luminescence Application**, ***Vincent Fernandez**,* IMN-CNRS, France*; Michel Féron,* LCC-CNRS, France*; Neal Fairley,* CasaXPS, France*; Myrtil Kahn,* LCC-CNRS, France*; Richard Clergereaux,* LPCE-CNRS, France*; Mireille Richard-Plouet,* IMN-CNRS, France

Due to their potential applications, white-light emitting materials have attracted extensive research interest. The covered fields of applications include information display, fluorescent sensors, and solid-state lighting. Among them zinc oxide with its photoluminescence characterized by two main bands: one related to excitons below 400 nm and a broad emission in the visible range could enable to obtain white light emission. In order to protect nanocrystalline phosphors such as ZnO nanoparticles (NPs) and keep their emission performance, a strategy is to embed them in transparent matrix. Among the possible oxides fulfilling the specification,

silica was identified as a suitable candidate thanks to its chemical stability and non-toxicity.

Nanocomposite (NC) thin films are prepared by a hybrid process [1] combining injection, at low pressure, of colloidal ZnO solution, forming an aerosol, in a Plasma Enhanced Chemical Vapor Deposition (PECVD) reactor.Thus innovative thin films consisting of ZnO nanoparticles and SiO_2 using this hybrid process were deposited by injection of nanoparticles stabilized by organic ligands and dispersed in 20%vol pentane-80%vol HMDSO solution in an Ar plasma. These films were characterized by XPS and by parallel Imaging energy scan XPS [2] on a Kratos Nova optimized instrument [3]. Data were analyzed using CASAXPS 2.3.27 [4]. Zn 2p, O1s, C1s and Si 2p Core levels were measured in parallel Imaging energy scan XPS with an energy resolution of 1.12 ±0.05 eV measured on Ag 3d5/2. Data analyses show anti-correlation between the atomic concentration of Zn, associated to ZnO nanoparticles, and both the atomic percentages of Si, associated to SiO_2 Fig 1 and the atomic concentration of Carbon fig 2. Moreover the energy resolution is good enough to map separately the amount the O bound to Zn, at 530.8 eV and the O linked to Si, at 532.6 eV.

These results highlight the possibilities offered by XPS imaging, allowing us to shed light on mechanisms involved during drying of the aerosol droplets at the substrate surface.

Acknowledgments

"Measurements were performed using the IMN's characterisation platform, PLASSMAT, Nantes, France."

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4:15pm **AS-MoA-12 Uncertainties in XPS Elemental Quantification***,* ***Alexander Shard****, Benjamen Reed, David Cant,* National Physical Laboratory, UK

X-ray photoelectron spectroscopy (XPS) is routinely employed to measure surface compositions. The standard approach to quantification treats the surface region as if it is homogeneous and applies sensitivity factors to measured peak intensities to calculate the 'equivalent-homogeneous composition' of the sample expressed as a mole fraction, which is usually converted to atomic percent. In this talk, we briefly summarise the main contributions to uncertainty in XPS composition measurements and provide mathematical expressions through which the uncertainty in the measured composition can be estimated and reported. Contributions to the measurement uncertainty from peak area measurement, detector linearity, sensitivity factors, spectrometer transmission and analytical practice are outlined and combined. We show that the statistical uncertainty in peak area measurement usually contributes negligibly to the accuracy of the measurement, but is the main factor that determines the precision. The best practices to improve the precision and accuracy of standard 'equivalent-homogeneous composition' XPS quantification are outlined.

4:30pm **AS-MoA-13 Revisiting Detector Linearity and Deadtime Correction for Photoelectron Spectrometers***,* ***Benjamen Reed****, Alexander Shard,* National Physical Laboratory, U.K.

In x-ray photoelectron spectroscopy (XPS) data, the integrated area under a core level peak is proportional to the atomic fraction of that element in the sample. Therefore, confidence in the intensity scale of a photoelectron spectrometer is vital for quantitative analysis. Sample dependent factors aside, the XPS analyst must calibrate for the relative intensity response (or transmission function) of their analyzer, which is largely a result of the 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 analyzer's detection system is correct. At high count rates, the photoelectron detector may exhibit non-linearity that significantly affects 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 and using high-throughput lens modes / 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. Awareness of this limitation of photoelectron detectors may not be universally known throughout the XPS users' community; in a recent VAMAS interlaboratory study on XPS intensity calibration, a number of datasets on sputter-cleaned gold were submitted that exhibited evidence of detector non-linearity.

With the international standard on detector linearity (ISO 21270) due for systematic review in 2026, it seems appropriate to revisit these concepts for the benefit of the surface analysis community. We present a method for assessing the linearity and deadtime correction of photoelectron detectors based on the *spectrum ratio* method from ISO 21270 with improved data selection criteria for multi-channel detectors. We also discuss the effect of non-linearity and incorrect deadtime correction on XPS quantification.

4:45pm **AS-MoA-14 Beyond the Standard Elemental Analysis of Surfaces - What more can be done with XPS?***,* ***Donald Baer,*** Pacific Northwest National Laboratory*; Merve Taner Camci,* Turkish Energy, Nuclear and Mineral Research Agency, Turkey*; David Cant,* National Physical Laboratory, UK*; Scott Chambers,* Pacific Northwest National Laboratory*; Hagai Cohen,* Weizmann Institute of Science, Israel*; Pinar Aydogan Gokturk,* Koc University, Turkey*; David Morgan,* Cardiff University and HarwellXPS, UK*; Andrey Shchukarev,* Umeå University, Sweden*; Peter Sherwood,* University of Washington*; Sven Tougaard,* University of Southern Denmark*; Sefik Suzer,* Bilkent University, Turkey*; John Watts,* University of Surrey, UK

Because of the importance of surfaces and interfaces in many scientific and technological areas, the use of XPS in publications has been growing exponentially. Although XPS is being used to obtain useful information about the surface composition of samples, much more information about materials and their properties can be extracted from XPS data than commonly obtained. This presentation describes some of the areas where alternative analysis methods or experimental design can obtain information about the near surface region of a sample, often information not available in other ways. Experienced XPS analysts are familiar with many of these methods, but they may not be known to new or casual XPS users and sometimes they have not been used because of an inappropriately assumed complexity. Information available includes, optical, electronic, and electrical properties, nanostructure, expanded chemical information and enhanced analysis biological materials and solid/liquid interfaces. Many of these analyses can be conducted on standard laboratory XPS systems, with either no or relatively minor system alterations. Topics discussed include i) Considerations beyond the "traditional" uniform surface layer composition calculation to obtain nanostructure of the near surface region, ii) using the Auger parameter to determine a sample property, iii) use of the D parameter to identify $sp^2$and sp^3 carbon information, iv) extracting phase and enhanced chemical information from the XPS valence band, v) using cryocooling to examine the solid/liquid interface and expand range of natural and biological samples that can be analyzed and minimize damage, and vi) Using electrical potential effects on XPS signals to extract chemically resolved electrical measurements including band alignment, electrical property information, double layer formation and charge dynamics.

5:00pm **AS-MoA-15 New in-situ capabilities of PEEM-3 endstation at the Advanced Light Source***,* ***Barat Achinuq,*** Lawrence Berkeley National Laboratory

For over a decade, the PEEM-3 endstation at the Advanced Light Source has been instrumental in numerous high-impact publications with wide range of topics including studies on magnetic and ferroelectric materials, two-dimensional materials, and biominerals, among others. In this talk, I will present recent additions to our sample environment. These include capabilities for measuring device structures at cryogenic temperatures, in-situ in-plane rotation at various temperatures, application of in-plane and out-of-plane magnetic fields, and radiation-based rapid heating. Coupled with a recent upgrade to our detector, these advancements open new avenues for exploration beyond our existing capabilities.

Applied Surface Science
Room 209 B W - Session AS-TuM

Surface Characterization of Energy Materials

Moderators: Jodi Grzeskowiak, TEL Technology Center, America, LLC, **Benjamen Reed**, National Physical Laboratory, UK

8:30am **AS-TuM-3 Solar Energy from a Big Picture Perspective to Nanoscale Insights via TOF-SIMS*, Steven P. Harvey,*** NREL **INVITED**

The world is rapidly changing the way that it gets energy due to rapid price declines in new energy sources and storage within the last ten years. We will briefly discuss solar energy trends as a whole, before diving into our recent contributions to the field using time-of-flight secondary-ion mass spectrometry (TOF-SIMS) at the National Renewable Energy Laboratory to improve the performance and reliability of solar cell and battery materials, and we will present some of our work that highlights the versatility of TOF-SIMS. This work includes: 1) Multi-scale, multi-technique investigations of photovoltaic module failure including TOF-SIMS to enable insights into the root-cause mechanisms of module degradation at the nanoscale that are observed at the length scale of meters 2) Investigations into the performance and stability of hybrid perovskite solar cell devices and our work to understand measurement artifacts in this materials class when profiling.

9:00am **AS-TuM-5 Introduction of Cryogenic X-Ray Photoelectron Spectroscopy for Chemical Analysis of Sensitive Battery Interfaces*, Sanzeeda Baig Shuchi,*** *Yi Cui, Stacey Bent,* Stanford University

Understanding the chemical environment of pristine interfaces is a long-sought goal in electrochemistry, materials science, and surface science. One such interface, the solid electrolyte interphase (SEI) in lithium battery anodes, is described as the nanometer-thick passivation layer between the lithium anode and electrolyte formed due to electrochemical and chemical decomposition of the electrolyte. For high performing electrolytes above ~95% Coulombic efficiency, SEI is considered the key performance modulator in next-generation lithium metal batteries.

Important understanding of the SEI is achieved using X-ray photoelectron spectroscopy (XPS). However, room temperature (RT) combined with the ultra-high vacuum (UHV) conditions of standard XPS can induce major SEI evolution from reactions and volatilization during measurement. Subsequently, a technique is necessary for SEI stabilization.

Here, for the first time, we develop cryogenic (cryo)-XPS with immediate plunge freezing and demonstrate SEI preservation. We show that cryogenic conditions can halt chemical reactions and freeze UHV-volatile species. Most chemical reactions are halted due to slow reaction kinetics at cryoT. We hypothesize that the true SEI thickness can also be retained, benefiting from the lower vapor pressure of different frozen SEI species at cryoT. Indeed, we discover completely different SEI composition and a thicker pristine SEI with cryo-XPS. While cryo-XPS ensures SEI preservation over an extended period under UHV, compositions derived from RT-XPS are dominated by stable species only. We confirm the SEI thickness preservation from Li 1s high-resolution spectra of the underlying metal substrate. We carefully analyze and decouple three major effects during SEI analysis: UHV effect, reaction effect, and beam effect. UHV and reaction are found to be the major drivers for SEI compositional changes under standard RT-XPS conditions.

While RT-XPS-based chemical descriptions fail to provide performance correlations, we show that pristine SEI composition achieved by cryo-XPS enables performance correlations across diverse electrolyte chemistries. We expect our research to inspire future studies of sensitive and reactive interface characterization under cryogenic conditions to ensure pristine state preservation.

9:15am **AS-TuM-6 Pulsed Laser Deposited-Ruthenium Dioxide Thin Films with Enhanced Electrocatalytic Performance for Energy Conversion Applications*, Ghanashyam Gyawali,*** North Carolina A&T State University

Ruthenium dioxide (RuO_2) is a promising material for advancing renewable energy solutions; however, its practical applications remain limited due to stability challenges and performance variations depending on the fabrication method. In this study, high-quality RuO_2 thin films were synthesized on crystalline sapphire substrates via the pulsed laser deposition (PLD) method. The orientation and crystallinity of the RuO_2 thin films were precisely controlled by adjusting the PLD growth temperature, and its impact on electrocatalytic performance was systematically investigated as the first part of this study. The structural and morphological properties of the films were characterized using high-resolution X-ray diffraction, X-ray reflectivity, X-ray photoelectron spectroscopy, scanning electron microscopy, and transmission electron microscopy, confirming epitaxial growth and high crystallinity. The second part of the study is focused on examining the effect of film thickness on the electrocatalytic activity and charge transfer behavior at the electrical double layer, enabling a comprehensive comparative analysis. Electrochemical characterization revealed a wide potential window with highly reversible redox reactions, indicating robust electrochemical activity. Furthermore, electrochemical impedance spectroscopy was conducted under varying applied potentials and different potassium hydroxide electrolyte concentrations to evaluate charge transfer dynamics. A comparative analysis of films with different thicknesses, controlled by varying the pulse number (4800 and 2100), demonstrated that thicker films with a higher pulse number exhibited superior electrocatalytic performance and enhanced stability. Notably, RuO_2 films grown at a pulse number of 4800 at 600 °C outperformed those fabricated at 2100, underscoring the significance of optimized deposition conditions. These findings highlight the potential of RuO_2 thin films as efficient and stable electrocatalysts, offering valuable insights for the advancement of energy conversion and storage technologies.

9:30am **AS-TuM-7 Surface and Bulk Characterization of Organic Semiconductors Using XPS and UPS Techniques*, Jonathan Counsell,*** *Liam Soomary,* Kratos Analytical Limited, UK*; Chris Moffitt,* Kratos Analytical Inc.

Organic semiconductors have gained significant attention in recently due to their potential for flexible, lightweight, and low-cost electronic applications. These materials, enable charge transport via delocalized electronic states, a characteristic of their π-conjugated molecular structures. Their utility includes various organic electronic devices, including Organic Thin-Film Transistors (OTFTs), Organic Light-Emitting Diodes (OLEDs), Organic Photovoltaics (OPVs), and organic diodes. The selection and performance of these materials depends on the semiconductor properties such as charge carrier mobility, energy level alignment, and stability [1]. Among the widely studied molecules, DNTT and CuPc function as p-type semiconductors, facilitating hole transport, whereas $CuF_{16}Pc$ serves as an n-type semiconductor, supporting electron transport. Additionally, F4TCNQ, a strong electron acceptor, is commonly employed as a molecular dopant to enhance the conductivity of p-type materials. Understanding the surface properties and chemical interactions of these molecules is crucial for optimizing device performance and stability.

We will explain the utility of a combination of experimental methods using a modern X-ray Photoelectron Spectroscopy (XPS) spectrometer (both small-area spectroscopy and 2D XP imaging) to probe the surface and bulk properties of both blanket and printed structures. This approach allows for an in-depth analysis of how organic semiconductors interact with substrates and templating/electrode layers. Additionally, we will explore the effects of deposition processes and the evolution of electrical properties as a function of depth, employing Hard X-ray Photoelectron Spectroscopy (HAXPES) and ion milling techniques. Furthermore, Ultraviolet Photoelectron Spectroscopy (UPS) will be utilized to determine the work function of these materials, a critical parameter in optimizing charge injection and transport. A methodological approach to surface characterization will also be discussed, providing insights into the interfacial properties that govern device performance.

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11:00am **AS-TuM-13 Investigations of the Solid-Electrolyte Interface in an All-Solid-State Battery Using ToF-SIMS*, Gabriel Parker,*** *Chanho Kim, Yaunshun Li, Guang Yang, Xiao-Ying Yu,* Oak Ridge National Laboratory, USA

Abstract: All solid-state batteries are a rapidly expanding field with complex formations of both the anode and cathode materials. Solid-state lithium sulfur batteries provide increased energy storage and improved safety. In this presentation, we investigate the composition and formation of the solid electrolyte interface (SEI) for pristine and cycled sulfur-based solid-state batteries. We compare two sulfide solid state electrolyte, namely, Li_6PS_5Cl (LPSCL) and $Li_{10}GeP_2S_{12}$ (LGPS).The cathode material composition is $LiNi_{0.8}Mn_{0.1}Co_{0.1}$ O_2 (NMC811). These nickel rich layered oxides provide contributions to energy storage and act as the active material offering high capacitance and voltage while the sulfide solid state electrolyte offers increased ionic conductivity. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was used to acquire surface spectra, depth profiles, 2D secondary electron (SE) images, and secondary ion 2D/3D images of the SEI. SIMS spectra and images were gathered using the 30 keV Bi_3^+ primary ion beam over a 500 × 500 µm² area for 60 scans. Depth

profiles were obtained using the 2 keV Cs^+ sputter beam and 30 keV Bi_3^+ primary ion beam over a 100 × 100 μm^2 area for 250 scans. Sulfur clusters (S_x) were observed, which were attributed to the deformation of the cathode surface after cycling. The mass spectral analysis and 2D/3D results imaged the SEI with formation of sulfates, phosphates and fluorine compounds. Comparisons of the LPSCL and LGPS in spectral analysis and 2D/3D imaging illustrate that LPSCL has higher counts of SEI formation products as well as indication of bubbling on the surface. In contrast, LGPS has pitting.Our results show that ToF-SIMS can uncover the mechanistic differences in SEI formation of all solid-state batteries.

Keywords: Solid-state batteries, solid-electrolyte interface, ToF-SIMS, sulfide solid-state electrolyte, imaging.

11:15am **AS-TuM-14 Study of the Solid Electrolyte Interface Formation at Hard Carbon Electrodes in Sodium-Ion Batteries**, *David Schaefer,* Justus Liebig University Giessen, Germany*; Sven Daboss, Christine Kranz,* Ulm University, Germany*;* ***Marcus Rohnke,*** Justus Liebig University Giessen, Germany

The performance and lifetime of sodium-ion batteries (SIBs) is determined by the interplay between material properties and solid electrolyte interphase (SEI) formation and evolution. The SEI enables electrochemical cells to function reliably and protects the cell from uncontrolled degradation.[1] It is formed primarily from electrolyte reduction products, with its main attributes targeted to be electric insulation, ionic conduction and stability against dissolution in the liquid electrolyte. Although the role of the SEI is recognized in the literature, its formation and evolution are not yet fully understood.[2]

This study focuses on the formation process and compositional evolution of the SEI on hard carbon composite anodes. The cells contain cyclic ester-based electrolytes including the additive fluoro ethylene carbonate and sodium metal counter electrodes. Morphological, chemical and electrochemical analyses were conducted at different sodiation potentials vs. Na^+/Na (unsodiated, 1.2 V, 0.9 V, 0.6 V, 0.2 V, 0.01 V) during the first half cycle, as well as during desodiation (0.3 V, 1.3 V, 2.0 V) until the end the first full cycle by scanning electron microscopy (SEM), time-of-flight secondary ion mass spectrometry (ToF-SIMS) and scanning electrochemical microscopy (SECM).

Starting from smooth particle surfaces in the pristine state, SEM revealed roughening during sodiation indicating SEI formation. Various visual representations of the SEI were obtained, showing a pox-, or bubble-like morphology. ToF-SIMS analysis revealed chemical differences at the surfaces between samples at different sodiation stages. An SEI consisting of the components Na_2O, NaOH, Na_2CO_3 and NaF with different compositions was observed by ToF-SIMS analyses of electrode surfaces, while oxidic components only seem to appear upon increased sodiation of the hard carbon composite electrode. Interestingly, the surface seems to have lost almost all oxidic residues after desodiation up to 2.0 V vs. Na^+/Na and regained sodium fluoride as the major residue salt component.

Information about changes in the electrochemical activity at the surfaces of the electrodes was obtained by SECM. Whereas pristine hard carbon particles are conductive and show a positive feedback signal this drastically changes upon formation of the SEI, hindering electron transport, which yields in a significant decrease in the electron transfer rate and a shift from positive to negative feedback response.

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11:30am **AS-TuM-15 Surface Sensitive Chemical Imaging of Lithium Materials for Battery Applications by Auger Electron Spectroscopy**, ***Juergen Scherer,*** Physical Electronics USA*; Masahiro Terashima, Kazutoshi Mamiya, Shin-ichi Iida,* ULVAC-PHI, Japan

Interest in all-solid-state batteries (ASSBs) has been increasing due to their higher safety, energy density, and longer lifespan compared to conventional lithium-ion batteries (LIBs). However, the internal resistance generated at the interface between the solid electrolyte (SE) and the electrode is a challenge for the practical use of ASSBs as it hinders fast charging and discharging. Several studies have been conducted to reduce the internal resistance through various surface modifications between the SE and cathode, which has led to a significant improvement in Li ion transport during charge and discharge. Despite the numerous studies on the SE/cathode interface of ASSBs, the mechanism behind the increase in interfacial impedance remains unclear.

In this study, we focus on lithium chemical mapping of the cross-section of the SE/cathode interface using Auger electron spectroscopy (AES). AES provides high spatial resolution information on chemical composition and state. The thickness of the anode, SE, and cathode layers in thin-film ASSBs is usually in the range of a few micrometers, making AES an ideal technique for obtaining chemical maps from solid-solid interfaces. Moreover, AES is more sensitive to changes in the lithium chemical state than X-ray photoelectron spectroscopy (XPS). However, it is well known that SEs are generally vulnerable to electron beam damage, and there are few reports on the application of AES in lithium mapping on SEIs.

We examine the electron beam damage on the surface of lithium phosphorus oxynitride (LiPON) as a model SE. The goal is to find the optimum conditions for AES lithium chemical mapping. To achieve this, the impact of electron beam damage on the LiPON surface was investigated. The results showed that the intensity of the LiPON peak was influenced by the beam energy, electron dose, and sample temperature. In conclusion, it was found that the optimal conditions for acquiring a lithium map are at room temperature using 3 keV electrons with a lower beam current.

With the optimum conditions, AES chemical mapping from the SE/cathode cross-section was conducted. Despite the challenges associated with lithium mapping using an electron beam, the study was successful in differentiating between the distributions of different chemical states of lithium in the form of LiPON and $LiCoO_2$. This was achieved through optimizing the beam energy, electron dose, and sample temperature. The results provide valuable insights into the lithium chemical distributions at the SE/electrode interface and contribute to a deeper understanding of the behavior of ASSBs at this interface.

11:45am **AS-TuM-16 Chemical and Elemental Analysis of Annealed Porous Transport Electrodes via X-ray Photoelectron Spectroscopy**, ***Lonneke van Eijk****, Jayson Foster,* Colorado School of Mines*; Lei Ding, Weitian Wang, Feng Yuan Zhang,* University of Tennessee Knoxville*; Adam Paxson,* PlugPower*; Svitlana Pylypenko,* Colorado School of Mines

Optimization of proton exchange membrane water electrolyzers (PEMWEs) is crucial for ensuring commercially competitive green hydrogen generation and facilitating the societal transition toward increased green hydrogen adoption. Current efforts focus on improving catalyst activity and stability by optimizing Ir oxide-based catalysts and developing alternative materials. Additionally, research aims to enhance catalyst layer (CL) structures and integrate them effectively with the titanium-based porous transport layer (PTL), which often includes a protective platinum coating. This work focuses on development of porous transport electrodes (PTEs) that integratemixed iridium-ruthenium oxide (IrRuOx) catalysts with Pt-coated titanium PTL. The complexity of the PTEs requires a multi-technique characterization approach that combines electron microscopy methods with X-ray photoelectron spectroscopy (XPS) for surface analysis and time-of-flight secondary ion mass spectrometry (ToF-SIMS) for surface and interface characterization.

This presentation will discuss XPS analysis of porous transport electrodes (PTEs) featuring IrRuOx catalysts that were subjected to various post-treatments involving annealing in different environments. The aim is to investigate how these parameters influence the material's composition and structure, and their respective impact on electrochemical properties. Emphasis is placed on the complexities of characterizing Ir-based materials, with detailed attention to the Ir 4f, Ru 3d, and O1s spectral regions. Due to difficulty of analysis of Ir 4f spectra, various fitting methodologies for O1s spectra were evaluated. It was found that some cases require detailed fitting analysis, while in other cases, basic metrics like binding energy and full width at half maximum (FWHM) are effective in capturing trends that are directly related to catalytic activity and stability. Additionally, XPS-derived metrics were correlated with electrochemical performance using Principal Component Analysis (PCA), highlighting patterns within complex data. These results advance our understanding of XPS analysis of complex catalysts, emphasize the importance of thorough and careful analysis, and highlight opportunities for combining simple metrics with multivariate analysis for the development of energy materials.

12:00pm **AS-TuM-17 X-Ray Photoelectron Spectroscopy Challenges: Practical Solutions to Peak Overlap in Battery Electrodes and Catalysts**, ***Lyndi Strange,*** Pacific Northwest National Laboratory*; Donald Baer, Mark Engelhard,* Pacific Northwest National Lab

X-ray photoelectron spectroscopy (XPS) is crucial for analyzing battery materials and catalytic systems. Several studies have indicated that XPS

analyses in the literature exhibit significant analysis flaws. One sometimes subtle but remarkably significant issue occurs when a minor peak significant component in a sample overlaps with a peak of interest and importance from an element of interst. This is particularly true with the amount of chemical state of “active” elements at lower concentration are the desired information. This talk highlights peak overlap issues that have been observed in our laboratory. We have focused attention on an often-overlooked F Auger overlap in Ni 2p spectra, relevant to battery anodes. This overlap occurs in many battery electrodes which because of the materials involved have complex photoelectron structures, including simpler elements like Li and F but also a variety of transition metals. We discuss challenges in XPS analysis of Li and nickel–manganese–cobalt (NMC) battery electrodes. Lithium analysis faces preparation challenges and peak overlap with F. New XPS users often overlook the interference of the FKLL Auger signal with the Ni 2p spectrum generated by AlKα X-rays in NMC electrodes. Simulated spectra of F and NiO demonstrate the extent of F Auger contributions to the Ni 2p signal, depending on the F/Ni atom ratio. This suggests how significant these effects are on the resultant spectra. Our analysis shows that overlap issues are significant for real electrode materials. We will also note other examples of peak interferences in quantification including the overlap of Ru 3d and C 1s in catalysts materials and how photoelectron structure from a TiO_2 support influence Pt 4f quantification for catalytic and energy conversion materials.

Applied Surface Science
Room 209 B W - Session AS-TuA
Theory and Data

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

2:15pm **AS-TuA-1 Distinguishing the XPS of Surface and Bulk Atoms*, Paul S. Bagus,*** University of North Texas*; Connie J. Nelin,* Consultant **INVITED**

Shifts in XPS binding energies (BEs), which reflect changes in the BE of an element in different environments within a given sample, have been extensively studied through both experimental measurements and theoretical approaches. These shifts are expected to provide insights into the physical and chemical properties of a system. To better understand the relationship between BE shifts and the properties of the ionized atom, we examine the mechanisms responsible for surface core level shifts (SCLSs). These shifts represent the differences between the BEs of surface atoms and bulk atoms. We will discuss the key mechanisms relevant to metals and ionic compounds (such as oxides), focusing on their similarities and differences. In particular, we will identify and distinguish the contributions of atomic charge and environmental factors - especially coordination and atomic distances - to the SCLS. One of the primary objectives is to establish the expected magnitudes of these shifts. The presented SCLS values are derived from ab initio wavefunctions for cluster models of the studied materials. Finally, we will compare the theoretical results with available experimental data to assess the accuracy and validity of the theoretical predictions.

2:45pm **AS-TuA-3 Theory as a Guide to Electrocatalysis: An Experimentalist's Point of View*, Jeffry Kelber,*** University of North Texas **INVITED**

In situ and *operando* XPS – in concert with experimental electrocatalysis and absorption spectroscopy – provide detailed understanding of interactions at the electrolyte/solid interface regarding studies of N_2 and nitrate reduction to NH_3 (NRR and NO_3RR, respectively). In such work, Hartree-Fock (HF)-based cluster calculations have provided specific interpretations of experimental near-ambient pressure XPS spectra, leading to important conclusions regarding the significance of stabilizing vanadium oxide cation surface sites in V(+3) oxidation states for NN and NO bond activation. DFT-based calculations have been critical in interpreting electrochemical and XPS data regarding NRR and NO_3RR reaction mechanisms – including the absence of the widely-supposed Mars van Krevelen mechanism in transition metal oxynitrides. Such DFT-based studies have also provided broad insight concerning catalyst reaction mechanisms, as well as the potential catalyst selectivity for, e.g., NRR vs hydrogen evolution. Thus, computational studies have served to not only better understand experimental results but also served as a strategic guide to future experimental studies.

Acknowledgement: This research was supported in part by the NSF under grant no. DMR 2112864 and is gratefully acknowledged. Additional support was provided by NSF support of the UNT CASCaM HPC cluster via grants CHE-1531468 and OAC-2117247 and is gratefully acknowledged.

3:15pm **AS-TuA-5 Fourier Denoising of XPS Data: An Algorithm for Automating the Identification of the Cutoff of the Gauss-Hermite Filter in Reciprocal Space and Feature Identification in XPS Spectra*, Alvaro J. Lizarbe,*** *Matthew R. Linford, Kristopher S. Wright, Garrett Lewis,* Brigham Young University*; David E. Aspnes,* North Carolina State University*; David J. Morgan,* Cardiff University, UK*; Mark Isaacs,* University College London*; Jeff Terry,* Illinois Institute of Technology*; Stanislav Průša,* Brno University of Technology

Introduction

Especially in X-ray Photoelectron Spectroscopy (XPS), large amounts of data and information are collected in its various modes that include imaging, depth profiling, stability, and operando studies. We recently published a paper[1] introducing Fourier analysis with a Gauss-Hermite filter function as a way to denoise X-ray Photoelectron Spectroscopy (XPS) data. While we always advocate for high quality data to be collected, Fourier analysis offers ways to improve collected data when the best possible signal-to-noise ratios cannot be obtained. Imperfect data are commonly obtained in sample damage studies due to changes in the sample, when elemental concentrations or low, when weak photoemission cross sections (seen in HAXPES) exist, when large numbers of spectra are collected in imaging studies, or when there is limited instrument time available. In such cases, Fourier analysis offers a mathematical approach to reduce noise and enhance signal quality, making it a valuable tool for XPS data analysis. We recommend that the original and smoothed data always be shown together. The Gauss-Hermite filter is a type of low-pass filter that applies a gradual, sigmoidal cutoff to low and high frequencies, allowing for a smooth transition between noise and signal. Currently, the position of this cutoff is adjusted manually by the analyst.

Work to be Presented.

The user must select the cutoff for the Gauss-Hermite filter we use to Fourier denoise XPS data. While the approximate location for this cutoff is generally clear from the shape of the Fourier coefficients in reciprocal space, it would be advantageous to be able to automate this process. In this talk, we describe an algorithm that successfully identifies the cutoff for the Gauss-Hermite filter, which should make this general approach to data denoising more widely applicable. This cutoff is based on statistical analyses of the fits. As a useful expansion to this capability, we show how this general approach can be applied when a high-order polynomial is used to fit carbon Auger data for D-parameter calculations.[2]

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4:00pm **AS-TuA-8 Fourier Denoising of XPS Data: Application of the Gauss-Hermite Filter Function to Carbon Auger D-Parameter, HAXPES, and LEIS data, and an Improved Algorithm for Reducing End-Point and Slope Discontinuity Artifacts*, Matthew R. Linford,*** *Alvaro J. Lizarbe, Kristopher S. Wright, Garrett Lewis,* Brigham Young University*; David E. Aspnes,* North Carolina State University*; David J. Morgan,* Cardiff University, UK*; Mark Isaacs,* University College London, UK*; Jeff Terry,* Illinois Institute of Technology*; Stanislav Průša,* Brno University of Technology, Czechia

A general trend in surface and material characterization is the collection of larger amounts of data and information. In X-ray photoelectron spectroscopy (XPS), large numbers of spectra are often collected in imaging, depth profiling, damage, and operando studies. These large quantities of data present challenges to the analyst who always has limited time for data analysis. Accordingly, mathematical tools for XPS data analysis should become more relevant and important, not less. We recently presented the case for the Fourier denoising of XPS data (Lizarbe, A. J.; Wright, K. S.; Lewis, G.; Murray, G.; Austin, D. E.; Terry, J.; Aspnes, D. E.; Linford, M. R. *J. Vac. Sci. Technol. A* **2025**, *43* (3)). The highest quality data should be collected whenever possible, and mathematical 'tricks' aren't, in general, a viable way to clean up extremely poor data. However, it's not always possible to collect data with the best possible signal-to-noise ratios. Imperfect data are often collected, when an element or chemical state of an element is present at a very low concentration, when cross section for photoemission is low, like in HAXPES, when many spectra must be collected in a short period of time, as in imaging studies, or when instrument time is simply expensive. For these reasons, noise removal from adequate data has a place in XPS data analysis. We showed that the traditional Savitzky-Golay and Boxcar smooths are lacking in their ability to successfully remove noise from data. These deficiencies, when observed in reciprocal space, demonstrate that these common smooths don't fully remove noise (high frequencies) from XPS data. A better approach to XPS data smoothing is with the Gauss-Hermite filter, which is applied in reciprocal space and has a sigmoidal shape. Below a user-selected cutoff, it preserves all the low-frequency information in a spectrum (low-index Fourier coefficients, signal), while removing high-frequency information.

In this talk, we describe an extension of these approaches to calculating the carbon Auger D-parameter and to smoothing HAXPES data. In addition, we show Fourier smoothing of data from a different technique: low-energy ion scattering (LEIS) data. LEIS spectra can present a challenge to data analysis because of their high sputter backgrounds at low energies. Finally, because numerical artifacts are introduced by Fourier denoising when there are end-point or slope discontinuities in the data, we show an improved algorithm for Fourier denoising via the Gauss-Hermite filter. This approach uses an improved function over what is currently in the software, which substantially reduces the current slope discontinuity in the current procedure.

4:15pm **AS-TuA-9 Identification of Materials from TOF SIMS Spectra via Machine Learning**, ***Lev Gelb****, Amy 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 complex and hard to interpret without expert knowledge, and investigate how machine learning might help. We primarily train models on simulated “big” data sets constructed by combining and modifying experimental spectra, with a focus on neural-network (NN) architectures.

Two applications are considered: identification of (presumed) homogeneous samples (which could be even a single pixel in a TOF SIMS image), and separation of multicomponent mixtures. In both cases, the sample consists of compound(s) which appear in some reference library, which is the basis for training. Complicating factors include statistical noise, background, calibration errors, and the likely case that the reference spectra were not taken under exactly the same conditions (primary ion, ion energy, instrument manufacturer, etc.) as the data to be analyzed.

In the first application, we focus on the extent to which improved spectral resolution helps (or hinders) analysis, the effect of reference library size on model performance, the effects of background counts and contamination by other species, and ways to have the model indicate that the sample is *not*described in the library. The NN approach is also compared with more straightforward spectral overlap-based methods and alternative machine-learning algorithms.

In the second application, the sample is assumed to consist of at least two components contained in the reference library. In addition to the complicating factors already mentioned, the presence of matrix effects can significantly complicate automated analysis. As in the first application, NN model performance is quantified and compared with overlap-based methods.

4:30pm **AS-TuA-10 Benefits of a Modern File Format for ToF-SIMS Imaging**, ***Alex Henderson,*** University of Manchester, UK **INVITED**

ToF-SIMS data is typically acquired into the proprietary file format of the instrument vendor. The vendor’s software has visualisation tools and data analysis routines that are tuned to that format, and that can be sufficient for the end-user. But what if we want to do something the vendor has yet to implement? What about those machine-learning or deep-learning AI methods we read about? Can we share our data with our collaborators? Can we publish it openly, as mandated by most academic funding providers?

Most vendors offer one or two data export options. Sometimes these are only suitable for single spectra, or images of pre-selected ions. Often the file format is something thought up by the vendor, or can be missing important metadata.

For SIMS there are only a limited number of open file formats, each with their limitations. Examples include ISO 14976 (the “VAMAS format”) for spectra and maps, and imzML, originally developed for MALDI, for hyperspectral imaging. Each of these has issues with the size of files generated by modern instrumentation, or modalities such as image depth profiling.

In this presentation we will explore formats from other ‘big data’ domains such as climate science and astronomy, to see whether these can be adapted to our data. In the course of this, we will explore peak detection, data compression, out-of-core data access, visualisation, and machine learning.

We will also present open questions regarding metadata and invite the community to be involved in the process of developing a common format suitable for our requirements.

Applied Surface Science
Room 209 B W - Session AS-WeM

Quantitative Surface Analysis II

Moderators: Hong Piao, FUJIFILM Electronic Materials USA., Inc., **Samantha Rosenberg**, Kairos Power

8:00am **AS-WeM-1 Using X-ray Photoelectron Spectroscopy to Determine Iron Oxidation State in Metamorphic Fe-Ti-oxides, Adirondack Mts, New York**, ***Jennifer Mann**, David Valley, Kateryna Artyushkova,* Physical Electronics; *William Nachlas, John Valley,* Department of Geoscience, University of Wisconsin

This presentation explores the application of X-ray Photoelectron Spectroscopy (XPS) for analyzing geological samples, specifically a rock sample from the Adirondack Mountains, N.Y. [1] The Adirondacks are notable due to their complex history and high-temperature metamorphic mineral compositions.These rocks represent the roots of an ancient mountain belt that have been exposed by uplift and erosion. The central Adirondack Highlands were metamorphosed, 1090 to 1020 million years ago, at pressures of ~0.8 GPa (depths of ~25 km) and temperatures up to 850 ºC, transforming the mineral-chemistry of many of the rocks. [2-3] The unique geochemistry provides an interesting test case for applying XPS analysis to this metamorphic transformation.

Of particular interest to geochemists is the ability to determine the Fe^{2+}/Fe^{3+} ratio in ilmenite and magnetite that can be used to infer peak-metamorphic temperatures.Traditional techniques like electron microprobe analysis have limitations in accurately differentiating these oxidation states. XPS, with its capability for detailed chemical state analysis, offers a promising complementary technique.However, Fe oxides are notoriously difficult to separate when multiple species are present, due to peak overlaps and changes in relative intensities of the satellite structure.[4] A library of Fe^{2+}/Fe^{3+} results for quantitative analysis is important for successful identification. In addition to a polished Adirondack rock sample, multiple hematite, magnetite, and ilmenite standards were measured.This library will be used to determine the oxidation states of iron within the rock's mineral phases.

The PHI *Genesis* has unique XPS capabilities in that it scans a focused (< 5 µm) X-ray beam across the sample surface.Using a combination of an optical image and PHI's unique scanning X-ray imaging capability, areas of interest on the petrographic thin section can be found quickly. The PHI scanning microprobe enables XPS analysis exclusively from ilmenite or magnetite sections of the rock. The Fe $2p_{3/2}$, Fe 3p, O 1s and valence band spectra from each of these two areas will be analyzed, by comparing relative intensities and binding energies of the peaks and satellite structures when present.

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8:15am **AS-WeM-2 Detection of Low Levels of Oxygen in Reactive Materials by X-Ray Photoelectron Spectroscopy (XPS)**, ***Jeff Shallenberger**, Robert Hengstebeck,* Pennsylvania State University; *Gilbert Rayner Jr.,* Kurt J. Lesker

Accurate detection of low levels of elements such as carbon and oxygen by ion beam sputtering techniques is complicated because those elements (as well as hydrogen) are the primary constituents of the residual gas molecules present in ultrahigh vacuum systems. In this paper we determine the minimum exposure of titanium to the vacuum is only 0.1 Langmuir (1 L = 10^{-6} Torr-sec) before detectable levels of adsorbed oxygen artificially raise the measured concentration. Despite this limited analytical window oxygen detection limits of 0.3-0.4 atom% can be achieved by x-ray photoelectron spectroscopy. We apply similar approaches to aluminum nitride and titanium nitride thin films grown by atomic layer deposition techniques to show best practices for detecting low levels of carbon and oxygen. A linear relationship between exposure and oxygen adsorption at exposures <4 L was observed for all materials studied.

8:30am **AS-WeM-3 Analysis Related Artefacts in the XPS Studies of MXEnes**, ***David Morgan***, Cardiff University, UK

MXenes are a class of two-dimensional inorganic compounds consisting of atomically thin layers of transition metal carbides, nitrides, or carbonitrides. MXenes possess excellent mechanical, electronic and optical properties, and consequently their application in a diverse range of scientific areas has been explored.

Given these intriguing properties, many XPS studies have been performed, resulting in critical analysis of the spectra and the decoupling of chemical state information therein, such as that in [1]. Further studies have shown that MXEne materials age in air with the growth of a TiO_2 phase and that controlled storage can inhibit or minimise such growth to times approaching 1 year of storage [2].

Herein it is shown that XPS analysis of these materials can lead to analysis induced changes at the surface, which to the best of our knowledge has not been previously reported and discuss strategies to minimise such changes and to extract meaningful analysis from damaged spectra.

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Acknowledgements

This work acknowledges the authors' provision of the EPSRC National Facility for Photoelectron Spectroscopy (HarwellXPS) under grant numbers EP/Y023587/1, EP/Y023609/1, EP/Y023536/1, EP/Y023552/1 and EP/Y023544/1.

8:45am **AS-WeM-4 Characterizing Oxide Phase Formation in Niobium-Based Superconducting Devices for NASA Astrophysics Missions**, ***Femi Akinrinola**, Vikum Dewasurendra, Seth Woodwyk, Aidan Sheppard, Matthew Johnson, Mikel Holcomb,* West Virginia University, USA

In NASA astrophysics missions, extremely sensitive detectors are required to capture faint signals from distant astronomical sources, particularly in the far-infrared to microwave regions of the spectrum. Emerging technologies such as microwave kinetic inductance detectors (MKID) and transition-edge sensors (TES) offer exceptional temperature resolution, yet their performance can be strongly influenced by the formation of unwanted oxide phases or other chemical changes during device fabrication. To address these issues, our research focuses on characterizing niobium (Nb)-based superconducting devices to identify and analyze the oxide phases forming on their surfaces. By integrating multiple material characterization techniques, we aim to understand how these oxide layers evolve and influence device performance. We utilize X-ray absorption spectroscopy (XAS) at synchrotron light sources to probe the near-surface region of the devices at nanometer-scale depths, providing detailed insights into the chemical states and electronic structure of niobium oxides. Our XAS analysis reveals the presence of multiple niobium oxide phases, including potentially metastable forms, which may play a critical role in degrading the superconducting properties of these detectors. X-ray photoemission spectroscopy (XPS) provides complementary support for these results. These findings help us correlate fabrication processes with the evolution of surface oxides, contributing to NASA's broader goal of optimizing detector performance for future space-based missions. This research is ongoing, and current efforts are focused on refining spectral fitting models, generating high-quality reference spectra for less stable Nb oxide phases, and enhancing the accuracy of phase quantification to better inform device design and fabrication protocols. We acknowledge support from NASA 80NSSC22M0173 and NSF 2417349.

9:00am **AS-WeM-5 Challenges in Next Generation Semiconductor Devices: Insights by Tof-Sims**, ***Rita Tilmann**, Alexis Franquet, Paul van der Heide,* IMEC Belgium **INVITED**

The semiconductor landscape is advancing, fuelled by evolvements such as the recently enacted European Union's Chips Act, promoting sustainability, and addressing the growing demand for higher performance in electrical devices. As the electrical industry increasingly prioritizes device miniaturization, there is a concurrent necessity for improved resolution metrology.

There is a marked expansion in the variety of applied materials that extend beyond traditional silicon leading to the integration of nanoscaled materials such as carbon nanotubes (CNTs) and two-dimensional (2D) materials like graphene and transition metal dichalcogenides (TMDs), as well as organic

and DNA-based electronics. This wide diversity at the nanoscale underscores the urgent need for advanced metrology techniques tailored to semiconductor device design.

Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) has emerged as a leading solution for addressing these metrology requirements. It offers the capability to analyze the composition and distribution of organic and inorganic materials at the nanoscale with exceptional precision. However, as the demands of semiconductor technology evolve, further improvements in TOF-SIMS methodologies are essential. Innovations such as the Self-Focusing SIMS (SF-SIMS) principle [1] and alternative erosion beam options, like oxygen gas cluster ion beams (O_2 GCIB), represent promising advancements. These enhancements can significantly improve the depth resolution and lateral precision of analyses for thin layered semiconductor stacked and patterned structures.

In this contribution examples of the new generation cFET analyses with TOF-SIMS including the beforementioned O_2 GCIB cluster in comparison to monoatomic O_2 and Cs beams is presented, finding the best compromise for increased depth resolution and sensitivity. In addition, the SF-SIMS principle is applied to enable quantification of Ge and dopants in SiGe layers.

As the industry moves forward, the focus on improving TOF-SIMS and related technologies will be vital enabling researchers and manufacturers to better characterize the increasingly complex nanoscaled materials and structures integral to next-generation semiconductor devices.

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9:30am **AS-WeM-7 XPS Investigation of Argon Monoatomic and Gas Cluster Ion Beam Etching of 4H SiC**, ***Ryan Raad,*** Christian Doppler Laboratory for Sustainable Silicon Carbide Technology, Institute of Sensor and Actuator Systems, TU Wien, Austria*; Markus Sauer,* Analytical Instrumentation Center, TU Wien, Austria*; Georg Pfusterschmied,* Christian Doppler Laboratory for Sustainable Silicon Carbide Technology, Institute of Sensor and Actuator Systems, TU Wien, Austria*; Ulrich Schmid,* Institute of Sensor and Actuator Systems, TU Wien, Austria

Depth profiling is commonly used in spectroscopic analyses, but it can significantly alter the chemical stoichiometry and crystalline structure due to ion-matter interactions, such as mixing, cascade collision, amorphization, or diffusion[1,2]. In compound materials like SiC, preferential etching worsens the overall situation, which can yield misleading analyses. The gas cluster ion beam (GCIB) technique has emerged as a promising solution, notably known for its low-damage irradiation[3]. However, sputtering parameters must be carefully tuned as even with this technique, destructive effects on inorganic materials were demonstrated[4]. Therefore, understanding the surface modification of innovative semiconductors such as 4H SiC is crucial to minimizing sputtering artifacts and ensuring accurate device analysis.

We investigated the sputter-etching behavior of Argon monoatomic and GCIB on the Si-face of monocrystalline 4H SiC samples. The surfaces were analyzed with XPS after 15 minutes of in-situ sputtering with Ar^+_n GCIB, followed by a 1-minute aggressive Ar^+ etching (4 kV, 1.9 µA) to magnify the contrast. Figures 1 and 2 show that increasing the energy and size of the cluster drastically changes the surface composition. As illustrated in Figure 1, for 2.5 kV 10 nA (blue) and 5 kV 20 nA (green), the oxygen signal undergoes a significant reduction only after switching to aggressive etching. We can assume that for a transferred energy of up to 3.8 eV/atom with a cluster of 1300 atoms, both the silicon oxycarbide (SiCxOy in violet at 101 eV on the Si 2p) and the 4H-SiC remain intact, while the adventitious carbon is sputtered away. However, when the impact energy is further increased

(10 kV 30 nA), the oxide is etched within the first 5 minutes (see Fig. 1) and the Si 2p detailed spectrum (see Fig. 2) broadens towards lower binding energy (Si-Si in red at 99.4 eV on the Si 2p). This reduction in the oxidation state of the silicon may suggest preferential etching of the oxide, as evidenced by a decrease in its FWHM value from 1.74 eV to 1.23 eV.

Acknowledgements

The financial support from the Christian Doppler Research Laboratory for Sustainable Silicon Carbide Technology is gratefully acknowledged, as well as the training and access to XPS from the Electrochemical Surface and Interface Analysis Cluster of TU Wien.

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9:45am **AS-WeM-8 Low Energy Ion Scattering Analysis of GC/IrO_x /SiO_2 Catalyst Layer Structures***,* *Philipp Brüner,* ***Thomas Grehl,*** IONTOF GmbH, Germany*; Rens Kamphorst, Katherine Encalada-Flores, Ruud Kortlever, Ruud van Ommen,* Delft University of Technology, Netherlands

Although atomic layer deposition (ALD) offers a precise method for growing ultra-thin coatings with sub-nm control due to its self-limiting nature, characterizing these films remains challenging for surface analytical techniques. This difficulty is particularly pronounced for ultra-thin films consisting of only a few atomic layers or even sub-monolayers, as most analytical methods lack sufficient surface sensitivity and often yield averaged information that includes both the deposited film and the underlying substrate.

In this study, we apply low-energy ion scattering (LEIS) to analyze SiO_2 films grown via ALD on an electrodeposited IrOx catalyst layer on glassy carbon (GC). LEIS records the energy spectrum of noble gas ions (He, Ne, Ar) scattered from the sample surface, where the elemental peaks correspond to the composition of the outermost atomic layer, enabling quantitative analysis [1]. This extreme surface sensitivity of just a single atomic layer combined with sensitive and quantitative elemental composition analysis is unique to LEIS, making it particularly valuable for investigating ultra-thin films. Additionally, signals from sub-surface scattering provide insights into sample composition and layer thickness up to 10 nm, depending on the material.

By leveraging both top atomic layer sensitivity and thickness information, we demonstrate how to quantify the surface coverage of SiO_2 films, detect surface impurities with high sensitivity, and assess the growth mode of the films. While ALD is often expected to produce films in a well-controlled layer-by-layer fashion [2], our results on these specific samples indicate varying degrees of island growth, where some regions of the substrate develop multilayer films early in the deposition process, while others remain largely uncoated. SiO_2 films grown using different ALD processes are presented, showing the differences in film formation depending on the growth conditions clearly picked up by LEIS.

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11:00am **AS-WeM-13 In situ and quasi-in situ characterization techniques for atomic-scale process development in device fabrication: focus on Area Selective Deposition process***,* ***Christophe Vallée,*** University at Albany-SUNY*; Marceline Bonvalot,* Grenoble Alpes University, France*; Remy Gassilloud,* CEA-Leti, France*; Cedric Mannequin,* University of Nantes, France*; David Muñoz-Rojas,* Grenoble Alpes University, France **INVITED**

In the recent years, innovative processes have enabled scaling nodes through the integration of new materials and new architectures at the nm scale. 3D NAND based on multi-layering needs highly selective process. The enhancement of DRAM from 1Y-1Z needs high aspect ratio processes. Sub 3nm logic development will need precision patterning process. Most of these requirements cannot be met without the use of atomically controlled processes. Hence, the latest generation of transistors need to integrate dozens of atomic layer deposition (ALD) steps and a few atomic layer etching (ALE) steps. The next generations will certainly include selective deposition steps with the use of an area selective deposition (ASD) process. An ASD process is designed to selectively deposit material only on a surface named growth area, with no deposition on a targeted surface named non growth area. This process can be carried out using chemical deposition processes, the most popular of which is ALD. It can also be coupled with an ALE etching process to form an ASD process by super-cycling od deposition and etch. Inhibitors can also be used to block the growth on the non-growth area. The processes described below require a perfect understanding and control of the interactions between molecules/radicals and surface chemical groups. This highlights the need for in situ and quasi-in situ techniques. In this presentation, we will address the methods most widely used to date. Then we'll look ahead to HVM applications, discussing

current needs in metrology, not only for process monitoring, understanding and control, but also for better measurement of process-induced defects and Yields.

11:30am **AS-WeM-15 Combining ISS, XPS and ion sputtering to discriminate Si-contamination from Si present in the stack of reticles for extreme ultraviolet (EUV) lithography***, **Véronique de Rooij-Lohmann**, Shriparna Mukherjee, Kleopatra Papamichou,* TNO, the Netherlands Organisation for Applied Scientific Research, Netherlands

EUV lithography scanners are extremely complex machines. The heart of the machine is formed by the optical system, which consists of a series of mirrors and reticle. To avoid loss of throughput and imaging performance, these need to remain free of contamination. In spite of great effort though, contamination is hard to avoid completely, as a result of the aggressive environment in combination with the plethora of components in the EUV lithography system.

Si – being ubiquitous in the semiconductor industry – is an element of particular interest to EUV-related optics Life-time research. XPS analysis of Si-contamination on optical samples (e.g. reticles and mirrors) is hindered though by the presence of Si in the sample stack. Because reference data from known clean samples is usually unavailable, the discrimination between Si as contaminant and Si as sample constituent relies on assumptions. Therefore, to advance this aspect of reticle metrology, we intentionally contaminated samples with Si, then investigated and compared several approaches to distinguish between Si on the surface and Si in the stack.

The metrology includes methods based on depth-resolved information from AR-XPS and HAXPES, Ion Scattering Spectroscopy as extremely surface-selective analysis method, and removal of the Si-contamination via mild etching with monatomic He^+, monatomic Ar^+, and Ar_{1000}^+ cluster ions. The suitability of these methods are first tested on model Ru- and absorber samples without Si in the stack. The most promising approaches are then applied to EUV reticles.

This project is supported by the Chips Joint Undertaking (under grant agreement No 101096772) and its members, including the top-up funding by The Netherlands.

Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or The Netherlands. Neither the European Union nor The Netherlands can be held responsible for them.

11:45am **AS-WeM-16 Using X-Ray Induced Auger Electron Spectroscopy Transitions to Explore the Surface Reactivity of Semi-Conductors***, Kirène Gaffar, Anna Gagliardi, Antonin Frappreau, Arnaud Etcheberry, Muriel Bouttemy, **Solène Béchu**,* CNRS, ILV, France

With the exception of the modified Auger parameter, X-ray induced Auger electron (X-AES) transitions remain underexploited to date. Indeed, they can provide a powerful insight for the chemistry evolution of semi-conductors (oxidation degree, chemical environment, atomic composition), as the classic photopeaks used in XPS. However, a direct interpretation (spectral signature, energy position) is not always straightforward or evident, requiring further data processing using specific decomposition procedures to take into account the complexity inherent in the shapes of these peaks.

The present work explores the decomposition of X-AES transitions by using two different methods of decomposition, the non-linear least square (NLLS) [1] and the linear least square (LLS) [2] methods. These are combined with principal component analysis and vectorial method [3]. The NLLS method requires multiple peaks to simulate the decomposition, which increases the potential for human error. However, minor adjustments can be performed with respect to position or FWHM values. In contrast, the LLS method employs a single envelope per chemical environment, which limits the decomposition error but excludes any small adjustments.

Following the implementation of different decomposition processes on Auger lines, three different applications of X-AES lines are presented. The first application involves the quantification of nitrogen in GaN material by XPS (performed with an Al Kα source), where the N 1s signal is overlaid with the Ga $L_2M_{4,5}M_{4,5}$ Auger line.[4] The second application is related to the kinetic aspect of the oxides formation of a solar absorber ($Cu(In,Ga)Se_2$ -CIGS- material). In order to explore similar depth probed (with an Al Kα source), Auger transitions and XPS photopeaks with similar escape depths are coupled for each CIGS element. This coupling method is also employed to study the surface reactivity of CdTe materials when exposed to air, with a specific input on the decomposition of Cd $M_{4,5}N_{4,5}N_{4,5}$ X-Auger lines.

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Chemical Analysis and Imaging at Interfaces
Room 205 ABCD W - Session CA+AS+SS-WeM

Chemical Analysis and Imaging at Interfaces Oral Session

Moderators: Andrei Kolmakov, National Institute of Science and Technology, **Xiao-Ying Yu**, Oak Ridge National Laboratory, USA

8:00am **CA+AS+SS-WeM-1 Heterogeneous Chemistry at Liquid-Vapor Interfaces Investigated by X-Ray Photoelectron Spectroscopy***, **Hendrik Bluhm**,* Fritz Haber Institute of the Max Planck Society, Germany **INVITED**

Aqueous solution-vapor interfaces govern important phenomena in the environment and atmosphere, including the uptake and release of trace gases by aerosols and CO_2 sequestration by the oceans. A detailed understanding of these processes requires the investigation of liquid-vapor interfaces with chemical sensitivity and interface specificity. [1] This talk will discuss opportunities and challenges for investigations of liquid-vapor interfaces using X-ray photoelectron spectroscopy and describe recent experiments that have focused on the propensity of certain ions and the role of surfactants at the liquid-vapor interface.[2-4] The talk will also discuss the utilization of photoelectron angular distributions for the investigation of the depth of solvation of surfactants at the interface. [5-7]

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8:30am **CA+AS+SS-WeM-3 Probing Chemical and Catalytic Interfaces Using Operando Soft X-Ray Spectroscopy***, **Jinghua Guo**,* Lawrence Berkeley National Laboratory **INVITED**

Synchrotron based X-ray spectroscopic techniques offers unique characterization of energy, catalysis and chemical process in regards to the functionality, complexity of material architecture and chemistry. In the operando soft X-ray spectroscopy study of interfacial phenomena, it has been found that the microstructure and composition of materials as well as the microstructure evolution process have a great influence on performances in a variety of fields, such as the energy conversion and energy storage materials in the chemical and catalytic processes. This presentation will show how to best use the X-ray spectroscopy characterization techniques, including X-ray absorption spectroscopy (XAS) and resonant inelastic X-ray scattering (RIXS) to investigate the real interfacial reaction mechanism during the operation. The experimental results show how operando soft X-ray spectra uncover the phase conversion, chemical and structure change of solid/liquid and solid/gas interfaces in real time, thus further enhance the understanding of real reaction mechanism.

9:00am **CA+AS+SS-WeM-5 Capturing Electrical Double Layer in Action with Xps on a Graphene Coplanar Capacitor with an Ionic Liquid***, **Sefik Suzer**,* Bilkent University, Chemistry Department, Ankara, Turkey

Time-dependent XPS data is recorded for capturing the dynamics of the Electrical Double Layer formation on electrified two Multilayered-Graphene electrodes, configured as a coplanar-capacitor, having an ionic liquid as the electrolyte. The device is subjected to 2 V biasing cycle changing its polarity every hour, while iteratively recording the O1s peak representing the anion with 0.5 s steps. Variations in the O1s peak's binding energy position on the electrified electrode report directly the electrical potential of the IL medium, which suddenly jumps to the opposite polarization, if the electrode is grounded. The peak eventually returns to its equilibrium position with a relatively long time constant. The complementing action is

also captured on the drain electrode, which exhibits mirrored but oppositely polarized temporal variations. Grounding the electrode allows separating the fast electronic components from those slow ionic ones, which is the key process introduced in this work, which is vital for better understanding of the function of the numerous components of the devices investigated. Experimental details will be given, these novel findings will be discussed and their implications for understanding the mechanism of the EDL formation will be presented.

9:15am **CA+AS+SS-WeM-6 Multimodal X-Ray Characterization of Materials Under Reaction Conditions*, Slavomir Nemsak,*** Lawrence Berkeley National Laboratory

Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) has established itself as a go-to technique to study heterogeneous and complex material systems under reaction environments. Multimodal approaches, which correlate information from two or more complementary techniques, are currently one of the forefronts of the APXPS development. In the past years, Advanced Light Source contributed one such setup: a combined Ambient Pressure PhotoEmission and grazing incidence X-ray Scattering (APPEXS) instrument commissioned and operated at beamline 11.0.2 The combination of the two in-situ techniques allows correlating structural and chemical information, which is critical for describing processes that transform materials in both these domains.

For example, by using APPEXS, we studied dynamics of the exsolution process of catalyst metallic nanoparticles [1], arrays of patterned nano-objects under reaction conditions [2], chemistry of ligands capping nanoparticles [3], discovered transformation of bimetallic nanoparticles during hydrogen storage process [4], and investigated CO_2 reduction catalyst under operating conditions [5]. Future developments of the technique and applications to a wider variety of scientific problems will be discussed.

[1] H. Kersell et al., Faraday discussions 236, 141-156 (2022)

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[3] M. Jaugstetter et al., ACS Nano 19, 1, 418–426 (2024)

[4] L.P. Matte et al., ACS Nano 19, 10, 10312–10322 (2025)

[5] G.Z. Girotto et al., arXiv preprint arXiv:2504.00350 (2025)

9:30am **CA+AS+SS-WeM-7 Ultrathin SiN_X Membrane Stability Under Energy Fluxes from Non-Thermal Plasma Discharges Monitored via Nanocalorimetry*, Carles Corbella,*** National Institute of Standards and Technology (NIST)/ University of Maryland, College Park*; Feng Yi, Andrei Kolmakov,* National Institute of Standards and Technology (NIST)

Freestanding ultrathin silicon nitride (SiN_x) membranes are widely used as electron, X-ray, and light transparent windows for environmental spectromicroscopy, separation membranes, and in microelectronics, e.g., as in MEMS devices and nanocalorimeters. However, their stability in the plasma environment requires further studies. Here, suspended 100 nm-thick SiN_x membranes have been wafer-scale fabricated on 15 mm^2-silicon frames using lithography. A platinum lithographically defined resistive microsensor of 100 nm thickness is deposited on the backside of the membrane, and it is calibrated for thermometry and calorimetry. This energy flux sensor (nanocalorimeter) has been exposed to cold plasmas in a custom-made research reactor equipped with a remote inductively coupled plasma (ICP) discharge source, Langmuir probe, retarding field energy analyzer, and optical emission spectroscopy (OES) channel. Energy fluxes (ions, electrons, energetic neutrals, and photons) from plasma plume are registered via sensor temperature evolution upon variations in the plasma parameters. The power carried by plasma species can be estimated from a simple energy balance model in measurements using sensor temperature variations up to a few hundred Kelvin with time resolution below 40 ms [Diulus et al, J. Vac. Sci. Technol. B 43, 020601 (2025)]. Additionally, the measurement setup allows for decoupling of the heating contributions by ions and VUV/UV-Vis-IR photons. It was found that the lifetime of the sensor is defined by the SiN_x sputtering rate combined with thermally induced mechanical stress. Ultrathin SiN_x membranes appear to be very robust even when immersed in the RF plasma plume region, manifesting low sputtering yield under typical electrically grounded experimental conditions. To investigate the chemical stability of the ultrathin membranes, nanocalorimetry experiments in argon plasma have been followed by preliminary tests using reactive gases such as oxygen and hydrogen.

9:45am **CA+AS+SS-WeM-8 Studying Tungsten and Alloys as Candidate Plasma Facing Material Using ToF-SIMS*, Xiao-Ying Yu,*** *Gabriel Parker, Tobias Misicko, Yan-Ru Lin,* Oak Ridge National Laboratory*; Tanguy Terlier,* Rice University*; Yutai Katoh,* Oak Ridge National Laboratory

Plasma facing materials (PFMs) are important in realizing fusion power. Tungsten (W) and alloys are considered primary candidates of PFMs due to their high melting points, high thermal conductivities, good neutron irradiation resistance, fast diffusion of hydrogen, low retention, and sputtering behaviors. However, technical challenges remain in adopting W and alloys as PFMs. In this presentation, we will share recent study cases of W and alloys using advanced microanalysis and chemical imaging, primarily time-of-flight secondary ion mass spectrometry (ToF-SIMS). SIMS is a powerful imaging mass spectrometry tool, and it can be used to reveal surface composition with high sensitivity or probe the material layer-by-layer and reveal spatial distributions in two-dimension or three-dimension. Due to parallel data acquisition, full spectral information consisting of elements, isotopes, and molecule permitted in the duty cycle is available in SIMS' chemical mapping. We will present a few case studies of potential PFMs using SIMS. First, High Flux Isotope Reactor (HFIR) irradiated single crystal tungsten (SCW) specimens from the FRONTIER collaboration campaigns were selected for spectral analysis and depth profiling. SCW coupons were subjected to shielded and unshielded neutron irradiation in HFIR. Prior to ToF-SIMS analysis, specimens were prepared using focused ion beam (FIB). To assure reliable peak identification and assignment, we performed analysis of pristine single crystal tungsten as a control. Mass spectra reconstructed from depth profiling show a variety of transmutation products in unshielded W, such as Rhenium, Osmium, and Tantalum. In contrast, not as many transmutation products were detected in the shielded irradiated W spectra. Second, W alloys were studied to verify the trace doping quantity of Boron (B) using the high mass sensitivity of SIMS spectroscopy, and measurements were verified using Raman. Depth profiling was used to verify the distribution of B within the W matrix. Third, we show that depth profiling with high spatial resolution can be used to map the grain boundaries in W alloys and assist the development of new materials and validate the engineering process. These recent studies provide results of the structural and compositional changes in W and alloys as potential PFMs, showing that SIMS can be a useful tool on elucidating alloy property changes and supporting material development for sustainable fusion in the future.

11:00am **CA+AS+SS-WeM-13 ToF-SIMS Acquisition Multiplexing - Concept, Applications, and Data Analysis*, Henrik Arlinghaus,*** 1) ION-TOF GmbH, Germany; 2) Institut für Hygiene, WWU, Germany*; Alexander Pirkl, Derk Rading, Julia Zakel, Ewald Niehuis,* ION-TOF GmbH, Germany **INVITED**

Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is a versatile technique for 2D and 3D analysis of surfaces. During the acquisition process, secondary ions are desorbed from the sample using one or more primary ion beams. These secondary ions are used to acquire a full mass spectrum at each voxel. Typically, a single acquisition mode is used when acquiring data, optimized for one specific potential aspect of the (unknown) sample. This becomes problematic when the number of acquisitions is constrained by the amount of sample available or the instrument time available. In the acquisition multiplexing approach, multiple acquisition modes, each of which is optimized for a specific performance aspect, are utilized during the acquisition process, resulting in multiple co-located datasets. Each of these acquired datasets may be analyzed individually in the traditional manner, or via algorithmic techniques such as Multivariate Statistical Analysis (MVSA) or Machine Learning (ML). Additionally, by taking advantage of the dataset's co-location property, it is possible to analyze all of the acquired data at once, finding aspects of the sample which span the data spectrally, spatially, and across acquisition modes.

We have applied this approach to vary numerous performance parameters of ToF-SIMS instruments, such as the primary ion beam current, the primary ion species, the focus of the beam, etc. Subsequently, analysis routines optimized for the parameter that was varied were applied to the datasets to make full use of the resulting data. One example is acquiring datasets using different primary ion beam currents, and then generating a High Dynamic Range (HDR) like dataset. High primary ion currents result in intense peaks which may saturate the detector signal. At the same time, low intensity signals are noisy at low primary ion currents. Another parameter which we varied is whether to optimize the primary beam for high mass resolution (and lower spatial resolution), or high spatial resolution (and lower mass resolution). This results in two datasets with fully complementary information. These may then be analyzed using machine learning based image fusion to generate a single high mass high

spatial resolution dataset.

11:30am **CA+AS+SS-WeM-15 Diamond Surface Analysis for Electronics and Quantum Applications***, **Alastair Stacey**,* Princeton Plasma Physics Laboratory **INVITED**

Characterising and controlling surface electronic and quantum states is an almost ubiquitous challenge for electronic and quantum technologies. The diamond material system is a particular example, where bulk states can be created with extreme purity but surface states, chemical and physical, are not yet well controlled or even understood.

In this presentation I will detail our efforts to analyse the diamond surface, with a variety of vacuum science techniques and theoretical analyses, and reveal some of the chemical challenges being faced in passivating and functionalizing this surface. I will show evidence that these surfaces remain significantly disruptive for quantum devices and present recent efforts in the development of high performance hydrogen terminated diamond transistors. Finally, I will forecast the remaining challenges and next steps for improving the surface science of this important quantum electronic material.

12:00pm **CA+AS+SS-WeM-17 ToF-SIMS Spectral Analysis Using Python***, **Tobias Misicko**,* Louisiana Tech University and Oak Ridge National Laboratory*; Nan Jiang, Xinghang Zhang, Yexiang Xue,* Purdue University*; Xiao-Ying Yu,* Oak Ridge Natinal Laboratory

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is a powerful surface analysis technique that enables spatially resolved chemical characterization of materials with high mass resolution and accuracy. However, analyzing ToF-SIMS data remains challenging due to the high dimensionality and large size of datasets resulting from parallel data acquisition. Previous efforts have largely depended on manual interpretation and the analyst's prior experience to apply dimensionality reduction techniques for material composition analysis. This process demands substantial human supervision and is hindered by the lack of open-source datasets and comprehensive, end-to-end code implementations for multivariate analysis pipelines, particularly for principal component analysis (PCA) and non-negative matrix factorization (NMF). In this work, we integrate both established and emerging methods tailored for ToF-SIMS spectral analysis, delivering an open-source, Python-based framework for intelligent mass spectral analysis to the ToF-SIMS research community. We demonstrate the application of PCA and NMF for spectral analysis and benchmark their performance using a quality-assured SIMS dataset.

Atomic Scale Processing Mini-Symposium
Room 206 A W - Session AP+AS+EL+EM+PS+TF-ThM

Advancing Atomic Scale Processing through Modeling and Simulation

Moderators: Heeyeop Chae, Sungkyunkwan University (SKKU), **Sagar Udyavara**, Lam Research Corp

8:00am **AP+AS+EL+EM+PS+TF-ThM-1 Multiscale Simulations for Atomic Scale Processing*, Michael Nolan,*** Tyndall Institute, Ireland **INVITED**

In modern semiconductor device fabrication, the dimensions involved require atomic level control over materials deposition and etch. Atomic Level Processing, exemplified by Atomic Layer Deposition (ALD) and thermal atomic layer etch (tALE), is therefore critical deposition and etch of relevant materials. Further scaling and use of complex three-dimensional structures means that Thermal ALE will take centre stage in etching. The key chemistry takes place at surfaces which drives the self-limiting characteristics and other advantages of these atomic level processing approaches. In this presentationt I will discuss how atomistic simulations based on first principles Density Functional Theory, ab initio Molecular Dynamics and kinetic Monte Carlo methods can be used to predict the chemistry of atomic level deposition and etch processes. I will first discuss the key chemistries involved in atomic level processing chemistries and the challenges that we have identified in this exciting area.The first scientific topic is the simulation of plasma enhanced deposition (PE-ALD) of metals, using the example of cobalt for next generation interconnects. This is the first example of an atomistic level study of the full PE-ALD cycle for Co metal and show that the process requires use of ammonia or mixed H2/N2 plasma. Calculated energy barriers for key steps give guidance regarding the temperatures required for the process. We show how substrate pre-treatment can reduce nucleation delay and therefore allow selectivity in deposition of the target film. Finally we show how kinetic Monte Carlo can be used to predict the structure of deposited metal films on different nitride substrates using data from DFT level simulations.The second example is molecular layer deposition of hybrid materials, using alucone as the prototypical example. Comparison of aliphatic with functionalized aromatic molecules allows differences in film properties to be understood. A further application of this involves selective, templated deposition of target films using block co-polymer infiltration where differences in reactivity of a precursor in two polymers promotes selective deposition of the target films. Finally, I present our work on self-limiting thermal atomic layer etching (ALE), highlighting how simulations can (1) predict the window of self-limiting etch (2) unravel the difference between amorphous and crystalline substrates and (3) probe the impact of surface orientation on tALE chemistry, all of which are important for future, selective thermal ALE processing on complex 3D substrates.

8:30am **AP+AS+EL+EM+PS+TF-ThM-3 The Si-Cl2-Ar+ Atomic Layer Etching Window: Fundamental Insights from Molecular Dynamics Simulations and a Reduced Order Model*, Joseph Vella,*** TEL Technology Center, America, LLC, USA*; David Graves,* Department of Chemical and Biological Engineering Princeton University

Plasma assisted atomic-layer etching (ALE) processes are frequently characterized by the ALE window. This is a range of ion energies where the amount of substrate etched remains constant as a function of the ion energy. Silicon (Si) etch by alternating exposure to chlorine gas (Cl_2) and argon ions (Ar^+) is frequently used as a demonstrative example to illustrate concepts of ALE, including the ALE window.[1] Despite this, when examining the literature, properties of the ALE window for this system remain obscure. For example, Kim et al.[2] studied Si-Cl_2-Ar^+ ALE and report that the ALE window should be below 40 eV. On the other hand, Park et al.[3] report the ALE window as being from 70 to 90 eV. Still others report an Ar^+ ion energy of 50 eV as being within the ALE window.[4] In this talk, we aim to resolve these contradictory reports by studying the Si-Cl_2-Ar^+ ALE with classical molecular dynamics (MD) simulations and a reduced order model (ROM).[5] The MD results show that the range of Ar^+ ion energies where the amount of Si etched per cycle (EPC) remains relatively constant is from 15eV to 20 eV, which is very narrow. The EPC in this region is also less than one atomic layer, because atomic Cl sputtering is significant. The results also show that a large ion fluence (roughly 4.2 10^{16} ions/cm^2 for 15 eV ions) is required to remove all Cl from the near surface region, which is a key insight when developing processes that achieve “true ALE”. Using the ROM, parameters can be varied to observe their effect on properties of the ALE window. For example, by increasing the threshold sputtering energy of Si, the width of ALE window can be increased. While this study focuses on the relatively simple Si-Cl_2-Ar^+ system, it is clear learnings from this study can be extended to other systems.

References

[1] T. Lill, “Atomic Layer Processing: Semiconductor Dry Etching Technology” (Wiley-VCH, Weinheim, 2021).

[2] B. Kim, S. Chung, and S. M. Cho, “Layer-by-later Etching of Cl-adsorbed Silicon Surfaces by Low Energy Ar^+ Ion Irradiation”, Appl. Surf. Sci. 2002, 187, 124-129.

[3] S. Park, K. Min, B. Yoon, D. Lee, and G. Yeom, “Precise Depth Control of Silicon Etching using Chlorine Atomic Layer Etching” Jpn. J. Appl. Phys. 2005, 44, 389-393.

[4] K. J. Kanarik, T. Lill, E. A. Hudson, S. Sriraman, S. Tan, J. Marks, V. Vahedi, and R. A. Gottscho, “Overview of Atomic Layer Etching in the Semiconductor Industry”, J. Vac. Sci. Technol. A, 2015, 33, 020802.

[5] J. R. Vella, Q. Hao, M. A. I. Elgarhy, V. M. Donnelly, and D. B. Graves, “A Transient Site Balance Model for Atomic Layer Etching”, Plasma Sources Sci. Technol., 2024, 33, 075009.

8:45am **AP+AS+EL+EM+PS+TF-ThM-4 Influence of Fluorination and Oxygenation Sources on the Thermal Atomic Layer Etching of MoS2*, Jacob A. Tenorio,*** *Icelene Leong, John D. Hues, Steven M. Hues, Elton Graugnard,* Boise State University

Atomic layer etching (ALE) has emerged as a pivotal technique in the precise fabrication of two-dimensional (2D) materials, particularly molybdenum disulfide (MoS_2), which holds promise in the semiconductor industry due to its high mobility in monolayer form. The ability to precisely etch amorphous and crystalline MoS_2 films provides a pathway for controlling thickness, which is critical to achieving desired electrical and optical properties. Previous studies used MoF_6 and H_2O in thermal ALE of MoS_2. Here, we report studies of alternate sources of fluorination and oxygenation and evaluate their impact on thermal ALE of MoS_2. Oxygen sources include water and ozone, and fluorine sources include HF/Pyridine and MoF_6. Etch rates, uniformity, and surface chemistry post ALE were characterized using spectroscopic ellipsometry, atomic force microscopy, and X-ray photoelectron spectroscopy. Results indicated at ALE of amorphous MoS_2 with HF with either H_2O or O_3 showed no signs of etching at 200 ºC or 250 ºC. Whereas the combination of MoF_6 + O_3 at 250 ºC on amorphous MoS_2 films exhibited an etch rate of 1.6 Å/cycle and a mass loss of 44 ng/cm^2. Further MoF_6 + O_3 etching at 200 ºC showed a mass loss of 19 ng/cm^2, similar to prior reports using MoF_6 + H_2O at 200 ºC. Surface morphology showed little change from etching, but surface oxygen concentration increased. This research further expands the capabilities for atomic layer processing of 2D materials.

9:00am **AP+AS+EL+EM+PS+TF-ThM-5 Insights Into Atomic Layer Etching of Diamond Surfaces*, Jack Draney,*** *Athanassios Panagiotopoulos, David Graves,* Princeton University

Thanks to its nitrogen vacancy color centers, diamond is a candidate for many quantum applications from quantum sensing to quantum computing. Pristine surfaces engineered for each application are required for good device performance. We investigated atomic-scale plasma processing as a method for reaching these pristine diamond surfaces. Our investigation takes the form of combined experiments and molecular dynamics simulations, allowing atomic-scale insights into the effects of argon / oxygen atomic layer etching on diamond surfaces.

9:15am **AP+AS+EL+EM+PS+TF-ThM-6 Benchmarking Large Language Models for Atomic Layer Deposition*, Angel Yanguas-Gil,*** *Matthew T. Dearing, Jeffrey W. Elam, Jessica C. Jones, Sungjoon Kim, Adnan Mohammad, Chi Thang Nguyen, Bratin Sengupta,* Argonne National Laboratory

In this work we introduce an open-ended question benchmark, ALDbench, to evaluate the performance of large language models (LLMs) in the field of atomic layer deposition. Our benchmark comprises questions with a level of difficulty ranging from graduate level to domain expert current with the state of the art in the field. Human experts reviewed the questions along the criteria of difficulty and specificity, and the model responses along four different criteria: overall quality, specificity, relevance, and accuracy. We ran this benchmark on an instance of OpenAI's GPT-4o using an API interface. This allows us to fine tune hyperparameters used by the LLM for text generation in a way that is not possible using conventional chat-based interfaces.

The responses from the model received a composite quality score of 3.7 on a 1 to 5 scale, consistent with a passing grade. However, 36% of the questions received at least one below average score. An in-depth analysis of the responses identified at least five instances of suspected hallucination. We also observed statistically significant correlations between the following question and response evaluation criteria: difficulty of the question and quality of the response, difficulty of the question and relevance of the response, and specificity of the question and the accuracy of the response. Finally, we will address other issues such as reproducibility, impact of hyperparameters on the quality of the response, and possible ways in which the performance of the LLMs can be further improved.

[1] A. Yanguas-Gil et al, J. Vac. Sci. Technol. A 43, 032406 (2025)

9:30am **AP+AS+EL+EM+PS+TF-ThM-7 Developing a "Digital Twin" for Area-Selective Deposition on 3D Nanopatterns***, **Nicholas Carroll**, Gregory Parsons,* North Carolina State University

Area-selective deposition (ASD)—a bottom-up patterning technique that enables precise material deposition on specific regions while preventing deposition elsewhere—has garnered significant attention as an augmentation to lithographic patterning of nanoscale features during semiconductor manufacturing. Some potential applications, such as contact-over-active-gate, will require multiple ASD materials to be deposited in sequence, heightening the challenge of effective process design. Given the vast time and resources required for experimental assessments of process integration, demand is rapidly growing for a "digital twin" (i.e. a software representation of a physical system) of device fabrication sequences. A comprehensive ASD digital twin will require advances in analyzing atomic layer deposition (ALD) reactor design and mechanistic insights into interactions between inhibitor molecules, ALD reactants, and substrate surfaces over time as reactions proceed.

We have recently developed a stochastic lattice model describing metal oxide ASD on planar substrates, including means to visualize the film shape and extent of lateral overgrowth during ASD.[1] Parameters in the model can be adjusted based on steric hindrance during each half-cycle, differences in interfacial energies between the non-growth surface and the growing film, and the preferred molecular bonding orientations. These factors elucidate subtleties in shape evolution during ASD, but results to date have been limited to vertical and lateral growth on 2D surfaces. A functional ASD digital twin must describe ASD on arbitrary 3D nanopatterns and on sub-lithographic feature sizes, including effects of selectivity loss where the selectivity decreases as film thickness increases.

We will present recent efforts in our group to extend the functionality of the stochastic lattice model to describe ASD on 3D substrates, including surfaces with pattern dimensions less than 10 nm. On very small features, for example, the model shows that lateral growth during ASD results in a wide distribution of feature separation distances, even when the growth per cycle is uniform across a growing film surface. We will also discuss intricacies that need to be considered to integrate multiple ASD steps into processes involving more complex "multi-color" substrates where several substrate materials exposed to reactants simultaneously. We believe that such insight will be critical for the realization of a functional digital twin model of atomic-scale processing needed for future semiconductor devices and other advanced manufacturing processes.

(1) Carroll, N. M.; Parsons, G. N. *J. Vac. Sci. Technol. A* **42** (6), 062411 (2024).

9:45am **AP+AS+EL+EM+PS+TF-ThM-8 Activation of C-X Bonds on Transition Metal Surfaces: Insight from DFT Studies***, **Matias Picuntureo**,* Universidad Tecnica Federico Santa Maria, Chile*; Ilker Tezsevin, Marc Merkx,* Eindhoven University of Technology, The Netherlands*; Scott Semproni, Jiun-Ruey Chen,* Intel Corporation*; Adriaan Mackus,* Eindhoven University of Technology, The Netherlands*; Tania Sandoval,* Universidad Tecnica Federico Santa Maria, Chile

Area-selective atomic layer deposition (AS-ALD) represents an advanced bottom-up nanofabrication technique enabling selective material growth on targeted areas of patterned substrates. In advanced semiconductor manufacturing, such as next-generation processes at the back end of line (BEOL), small molecule inhibitors (SMIs) can enable AS-ALD through the selective formation of inhibitor layers on metal surfaces that block deposition.

A recent study by Merkx et al. reported hydrogenolysis and potentially dehydrogenation of aniline on Ru surfaces during AS-ALD, leading to the formation of a carbonaceous layer with enhanced inhibition performance. This highlights the importance of understanding the driving forces behind the surface chemistry of SMIs.

To explore whether similar surface-mediated reactions can occur for other inhibitor–metal combinations, we employ density functional theory (DFT) to investigate the adsorption and dissociation mechanisms of benzene-derived SMIs on Ru(0001), Mo(110), and W(110) surfaces.

To enable a systematic comparison across different molecules and surfaces, our study focuses on radical-mediated dissociation pathways involving the cleavage of functional groups from the aromatic ring. This approach allows us to isolate the effect of the functional group and its interaction with the metal surface in determining the reaction thermodynamics between the molecular and dissociated adsorbed states.

We find that charge transfer to the adsorbed inhibitor modulates its dissociation energy landscape. The resulting radical intermediates are substantially stabilized through coordination with the metal surface. We further explore their subsequent hydrogenation, which transforms these surface-bound radicals into more stable, saturated species. Lastly, we show that the fate of reaction by-products—whether they remain adsorbed or desorb into the gas phase—can significantly impact the overall reaction thermodynamics and shift the equilibrium toward or away from product formation.

The investigation of the reaction pathways explored in this study contributes to the fundamental understanding of molecule–surface interactions during AS-ALD and offers insight that may support future strategies for the rational design of small molecule inhibitors.

References:

[1] Merkx et al., J. Chem. Phys. 160, 2024.

11:00am **AP+AS+EL+EM+PS+TF-ThM-13 Descriptor-driven analysis of inhibitors for AS-ALD processes***, Joost F. W. Maas, Marc J. M. Merkx,* Eindhoven University of Technology, Netherlands*; Matías Picuntureo, Lucas Lodeiro,* Universidad Tecnica Federico Santa Maria, Chile*; Adriaan J. M. Mackus,* Eindhoven University of Technology, Netherlands*; **Tania E. Sandoval**,* Universidad Tecnica Federico Santa Maria, Chile

Area selective atomic layer deposition (AS-ALD) is a bottom-up technique that can address some of the challenges that limit the nanofabrication of complex structures, which require patterning and alignment at the atomic scale. Currently, one of the most robust strategies to carry out AS-ALD is with the use of small molecule inhibitors (SMIs), that selectively adsorb and inhibit the non-growth surface (NGS) and prevent precursor adsorption. These SMIs range from a variety of functionalities and structures depending on the target NGS, and their selection is based on specific criteria, such as reactivity, volatility, and safety.[1,2]

Currently, the library of tested inhibitor molecules is very limited, therefore finding the best candidate for a given surface is challenging. Using computational tools can significantly accelerate the expansion of this library through high-throughput screening and recent advances in machine learning. In the case of the use of descriptors,[3] the goal is to correlate the performance of the SMIs e.g., measured in terms of their stability, as adsorption energy, with the dependence on materials or molecular properties. The derived correlations can serve to establish general guidelines for SMI selection, expanding the analysis to other molecules not included in the initial study. This approach has proven to be very successful in reducing computational costs in other fields, such as heterogeneous catalysis and drug discovery.

In this presentation, we provide an overview of the dependency between a list of descriptors and the adsorption energies of SMIs candidates on a variety of relevant NGS, such as oxides, nitrides, and metals. We explore descriptors based on the molecular properties, such as electronegativity, electrophilicity, and orbital energy, as well as descriptors based on the electronic structure of the material, such as d-band center. Results indicate a with strong correlation with the adsorption energy (E_{ads}) and electronegativity of the core-atom on the adsorption of oxides and nitrides, as well as the d-band center on the adsorption on metal surfaces. Moreover, our data highlights the differences in reactivity across surfaces and the challenges in surface passivation across surfaces with similar surface sites. Overall, this study provides important insights into the use of descriptor-driven analysis in the selection of the right SMI candidates for the advancement of ASD processes.

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[2] P. Yu, et al. *Appl. Surf. Sci.* 2024, 665, 160141.

[3] C. Chen, et al. *J. Phys. Chem. C* 2025, 129, 13, 6245–6253.

11:15am **AP+AS+EL+EM+PS+TF-ThM-14 Understanding Plasma-Induced Bonding and Composition Changes in SiCN ALD via kMC–DFT Modeling***, **Ting-Ya Wang**,* University of Texas at Austin*; Hu Li, Peter Ventzek,* Tokyo Electron America*; Gyeong Hwang,* University of Texas at Austin*; Jianping Zhao,* Tokyo Electron America

Plasma-enhanced atomic layer deposition (PEALD) enables low-temperature processing of silicon carbonitride (SiCN), a critical low-k material for advanced interconnects. However, energetic plasma species—including both ions and radicals—can significantly influence surface reactions, film composition, and structural evolution, ultimately affecting material properties such as dielectric constant and mechanical strength. A comprehensive understanding of these species-specific effects is essential for process optimization.

Integrating kinetic Monte Carlo (kMC) with density functional theory (DFT) offers a powerful approach for simulating ALD. However, a key challenge in kMC lies in the need for a predefined list of permissible events. Traditionally, researchers manually compile a set of reactions deemed most significant. Yet, the vast number of possible events on a surface, combined with the importance of rare events in ALD, raises concerns about the authenticity and completeness of outcomes derived from manually curated reaction lists.

To address this, we developed an atomistic, off-lattice, three-dimensional simulator that integrates kMC with DFT. We employed a strategic approach to construct a comprehensive event list, capturing a broad spectrum of potential surface reactions. This year, we expand our study in four key directions: (1) comparison of ion- and radical-driven reaction pathways to delineate their distinct roles in modifying surface chemistry; (2) evaluation of different plasma chemistries (e.g., N_2 vs. NH_3) to understand how reactive species impact film stoichiometry and termination; (3) simulation of multi-cycle growth to track the evolution of defects and compositional shifts; and (4) simulation predictions against experimental data such as XPS and IR spectra.

Our findings reveal a synergistic interplay between ions and radicals in shaping the formation of Si–N, Si–C, and C–N bonding networks. The simulation platform enables insights into plasma–surface interactions, offering a predictive framework for optimizing SiCN PEALD processes.

11:30am **AP+AS+EL+EM+PS+TF-ThM-15 Understanding SiCN Film Oxidation Mechanism Through Density Functional Theory***, **Tsung-Hsuan Yang**, Hu Li, Jianping Zhao, Peter Ventzek,* Tokyo Electron America

Low dielectric constant (low-k) spacers are essential components in advanced microelectronic devices for mitigating parasitic capacitance and crosstalk, leading to enhanced device performance. Among low-k materials, silicon carbon nitride (SiCN) is widely used for its tunability in dielectric constant, leakage current and chemical robustness. However, the long-term stability of SiCN films is often compromised by atmospheric moisture, leading to the formation of silicon oxide. To address this issue, we utilize density functional theory (DFT) to elucidate the fundamental oxidation mechanisms of SiN and SiC components by H_2O. Reaction rates were estimated with a combination of transition state theory and Arrhenius equation, enabling prediction of oxidation rates under various processing conditions. Additionally, H_2O diffusion within SiCN films was modeled, demonstrating a direct correlation between film density and oxidation kinetics. More importantly, the findings in this work can be applied in depositing SiOCN film as the oxidation mechanisms are predicted to be similar with other oxidation agents. Knowledge of these oxidation mechanisms enables precise control of the SiOCN film deposition process, facilitating component tunability.

11:45am **AP+AS+EL+EM+PS+TF-ThM-16 From Bulk Titanium Nitride to Small Molecule Inhibitors: a DFT Study Aiming Towards Area-Selective Atomic Layer Deposition***, **Lucas Lodeiro**,* Universidad Tecnica Federico Santa Maria, Chile*; Marc J. M. Merkx,* Eindhoven University of Technology, The Netherlands*; Dennis M. Hausmann, Rachel A. Nye de Castro,* LAM Research*; Adriaan J. M. Mackus,* Eindhoven University of Technology, The Netherlands*; Tania E. Sandoval,* Universidad Tecnica Federico Santa Maria, Chile

Titanium Nitride (TiN) is a hard and inert ceramic used as a protective coating, and in microelectronics for its metallic behavior. TiN thin films improve devices performance as conductive connection and diffusion barrier, and can be further functionalized to promote specific applications. Atomic Layer Deposition (ALD) enables precise TiN film deposition, with temperature controlling crystal growth facet. However, achieving area-selective ALD (AS-ALD) on TiN is challenging, because the lack of information of surface groups present in deposited TiN, requiring reliable surface models to search for solutions for precursor selectivity and inhibition with Small Molecule Inhibitors (SMIs) at atomic scale.

This study uses Density Functional Theory (DFT) to examine TiN surface properties, crystal facets, and surface chemistry. It also explores the adsorption of various organic and inorganic precursor (Al, Si, Ti-based) and SMI (aryl, aldehyde, and nitrogen-based) molecules on TiN with the aim of studying their potential for AS-ALD processes with TiN as growth or non-growth area.

Our findings on crystal facets align with experimental data, showing the (001) facet is the most stable, followed by the (111) facet, which is observed at high deposition temperature.[1] The reactivity and functionalization strategies of these surfaces differ significantly. The (001) surface shows low reactivity (especially with H_2O, NH_3, and H_2), resulting in bare surface sites.[2] Conversely, the (111) surface is reactive and can undergo hydrogenation, altering its electronic properties.

The differences in electronic surface properties significantly affect surface chemistry and the adsorption mechanism of the different molecules. The (001) surface exhibits metallic behavior, with strong interactions with various functional groups (for example, -1.8 eV for Benzaldehyde, BA), similar to copper surfaces.[3] In contrast, adsorption on the (111) surface is weaker and mainly dispersive (-0.8 eV for BA), highlighting the importance of the TiN film facet. Experimental findings show enhanced inhibition of BA and higher selectivity for low temperature deposited TiN, which could indicate the presence of the (001) surface, and a more stable inhibitor adsorption.

The key findings of this study offer valuable insights into surface reactivity and electronic properties to use TiN in AS-ALD process. Ultimately, this work aims to provide insights into controlling TiN deposition at the nanoscale, opening avenues for advanced microfabrication and surface engineering applications.

[1] Met. Mater. Int. 2001, 7, 621–625.

[2] J. Phys. Chem. C 2013, 117, 38, 19442–19453.

[3] Chem. Mater. 2025, 37, 1, 139–152.

12:00pm **AP+AS+EL+EM+PS+TF-ThM-17 Trimethylaluminum Reactivity on SiO_2 Surfaces at Cryogenic Temperatures – Implications for Al_2O_3 ALD***, **Leonhard Winter**, Ravi Ranjan, Francisco Zaera,* University of California, Riverside

The atomic layer deposition (ALD) of aluminum oxide films on solid substrates using trimethylaluminum (TMA) and water is often considered a prototypical ALD process. Several investigations have attempted to understand the mechanistic details of this deposition by following the corresponding steps *in situ* under reaction conditions. To gain a more fundamental understanding, we have set out to study this system following a UHV surface-science approach, slowing down the reaction, decreasing the gas exposures and substrate temperature, and following the progress of the reactions using surface science techniques. We chose to study this chemistry on SiO_2 films grown *in situ* onto a Ta support because SiO_2 is one of the most common substrates in the microelectronics industry.

We investigated the adsorption and reaction of TMA with SiO_2 by using X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD). We found that TMA starts to react with the SiO_2 surface at ≈110 K, i.e. below the cryogenic temperatures required for multilayer condensation. This low-temperature chemistry appears to be complex, as multiple reaction pathways can be deduced from analysis of the TPD data. In addition to the expected product methane, we observed the formation of ethylene and heavier fragments, probably also containing Al. The complex behavior of TMA on SiO_2 is not limited to low temperatures, as the loss of alkyl groups continues over several hundred kelvins upon heating of the sample. Isothermal adsorption experiments show that at room temperature the TMA uptake is self-limiting with an initial sticking coefficient that is approximately 4-5 times smaller than at cryogenic temperatures, where multilayer growth occurs. To model ALD-type growth, we alternately dosed TMA and water at 200 K and followed the chemical composition of the surface with XPS. The results are in agreement with the expected ALD behavior, which shows that ALD growth is possible at these extremely low temperatures for the TMA/water system. The two precursors were also co-dosed in a CVD-type deposition, which results in the growth of multilayer films of aluminum oxide on the SiO_2 substrate. Surprisingly, the growth was observed to proceed faster at 200 K than at room temperature, which we explain by a kinetic effect of prolonged residence times of the precursors at lower surface temperatures.

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AS-ThP-1 EUV Induced Degradation Studies on Reticles by XPS, ***Shriparna Mukherjee**, Alessandro Troglia, Véronique de Rooij-Lohmann,* TNO Science and Industry, the Netherlands

EUV reticles play an important role in the semiconductor manufacturing since their quality directly impacts the resolution and accuracy of the transferred image onto the wafer. This, in turn, affects the performance and yield of the resulting chips. Meanwhile, these reticles are very costly and subject to degradation. Better understanding of degradation mechanisms is therefore necessary to improve the designs and further increase the life-time. Under the framework of the European project 14ACMOS, TNO develops metrology for reticle degradation assessment. Test samples are produced for metrology studies by inducing degradation on various types of reticles. One of the criteria is that the degradation should be non-reversible upon exposure to the ambient, as the samples will be transported to metrology equipment in ambient conditions. Also, it is preferred to have lateral variations and real EUV-induced degradation. Different types of reticles (multilayer blank, absorber blank, patterned reticles) were exposed to EUV at TNO's EUV beam line 2 (EBL2). To facilitate oxidation, water and oxygen were introduced into the exposure chamber. XPS analysis was performed before and after the EUV exposures. Severe oxidation of Ru and Si were primarily observed on the multilayer blank. Moreover, compared to the pre-XPS, the post XPS analysis showed significant decrease in Ru while no such decrease was observed in case of Mo/Si. This might indicate that EUV induced oxidation resulted in intermixing or surface segregation and delamination in the multilayer blanks.

AS-ThP-2 Advanced Characterization of Sputter Induced Effects on the Work Function Using a Combined ToF-SIMS/SPM Instrument, *Bertram Schulze Lammers, Julia Zakel, Andreas Pelster, Derk Rading,* ***Thomas Grehl,*** IONTOF GmbH, Germany

The work function is the minimum energy required to remove an electron from a solid surface. This quantity can be directly related to the Fermi level which is of major interest for solid-state physics, material science, and semiconductor applications. Kelvin Probe Force Microscopy (KPFM) combines Scanning Probe Microscopy (SPM) with the electrostatic Kelvin probe method. It can laterally resolve the work function difference between the probing tip and the sample surface together with the corresponding surface topography.

Although the work function describes a macroscopic property of a solid, it may vary locally due to doping, surface contamination or surface oxides. Therefore, clearly defined measurement conditions are required to avoid artifacts and to gain reliable results.

For this work, a combined instrument for time-of-flight secondary ion mass spectrometry (TOF-SIMS) and SPM is used. It enables working under clean UHV conditions, preparation and measurement take place completely in-situ. As mentioned above, the work function of the sample is not measured absolutely but relatively to the probing tip. Once the chemical termination of the tip changes due to e.g. wear or oxidation, the reference is changed, and a general comparison is not possible anymore.

Furthermore, the resulting voltage differences from varying work functions causes additional contributions to the tip-sample force interaction leading also to artifacts in topography measurements. This variation may be sample specific but can also be artificially induced by the ion beam. Separating the work function effect from the topography signal enhances the reliability of the SPM results.

For comparative studies or quality control purposes it is mandatory to control the reference, determined by the termination of the tip. This can be achieved by in-situ tip cleaning, as is performed by the ion sources of the TOF-SIMS. The ion milling removes unknown contaminations and potentially sharpens the tip apex, resulting in a well-defined tip as a reproduceable reference.

As a model system, a silicon wafer is bombarded with different doses of different ions, to compare the effect on the work function. Known tip and sample conditions allow a clear correlation between work function variations and the ion bombardment to characterize the sputter induced effects on the work function.

This work demonstrates the possibilities of KPFM for the investigation of implants, doping or compound semiconductors. In addition, it aims at separating the effects of the work function in topographic measurements and therefore remove artifacts.

AS-ThP-3 Effect of Pulse Duration and Multi-shot Ablation in Femtosecond Laser Ablation (fs-LA) XPS Depth Profiling of Indium Phosphide, ***Charlie Chandler,*** University of Surrey, UK*; Dhilan Devadasan, Simon Bacon, Tim Nunney,* Thermo Fisher Scientific, UK*; Mark Baker,* University of Surrey, UK

Femtosecond laser ablation (fs-LA) is a newly developing XPS depth profiling technique which avoids the chemical damage observed using traditional monatomic and gas cluster ion beam sputtering [1]. The laser pulse duration plays a key role in determining the involvement (or not) of thermal processes in the ablation mechanism. InP is a thermally sensitive compound semiconductor material, as shown by enhanced preferential sputtering effects being observed when profiled using a gas cluster ion beam compared to a monatomic ion beam [1]. As such, it is a useful test material for studying the effects of laser pulse length on chemical composition during profiling. fs-LA XPS depth profiles of bulk InP were recorded using a 1030 nm laser for pulse durations varying between 160 fs and 6 ps. To ensure the true chemical composition could be retained at ultrashort pulse lengths, a multi-shot regime at a laser energy below the ablation threshold was required. The effect of laser pulse duration and variation of the number of shots per ablation level on the chemical composition, ablation threshold energy and crater surface morphology during profiling will be presented and discussed.

[1] M.A.Baker et al, Applied Surface Science 654 (2024) 159405

AS-ThP-4 Applications of Femtosecond Laser Ablation (fs-LA) XPS Depth Profiling, ***Mark Baker,*** *Charlie Chandler,* University of Surrey, U.K.*; Simon Bacon, Dhilan Devadasan, Adam Bushell, Tim Nunney, Richard White,* Thermo Fisher Scientific, UK

XPS depth profiling is widely employed to determine the chemical composition and offer chemical state information for thin films, thin film devices, coatings, surface treatments and surface degradation processes. Traditionally, XPS depth profiling has been performed through sputtering, using a monatomic or gas cluster ion beam (GCIB). However, many materials suffer from ion beam induced chemical damage during profiling, resulting in distorted chemical compositions and incorrect chemical state information being recorded during the depth profile. Recently, in a new approach to XPS depth profiling, ion beam sputtering has been replaced by femtosecond laser ablation (fs-LA). This new methodology has been shown to offer significant advantages over sputtering: (i) avoidance of chemical damage; (ii) profiling to much greater depths (several 10s microns); (iii) faster profiling speeds; (iv) ease of varying the ablation rate for different materials [1]. Using a 1030 nm wavelength, 160 fs pulsed laser, fs-LA XPS depth profiles will be shown for selected thin films, coatings, devices, surface treatments and oxidised surfaces, demonstrating the capabilities of this new technique.

[1] M.A.Baker et al, *Applied Surface Science* **654** (2024) 159405

AS-ThP-5 Standardless, Semi-quantitative ToF-SIMS depth profiling using the Full Spectrum Method (FSM), ***Nicolas Molina Vergara,*** University of Texas at Austin*; John Curry, Tomas Babuska,* Sandia National Laboratories*; Filippo Mangolini,* University of Texas at Austin

The quantitative evaluation of the depth-dependent chemical composition of thin films plays a pivotal role in the development of novel technologies across several sectors, from electronics to medicine. While Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) offers exceptional chemical sensitivity and spatial resolution as well as the possibility of acquiring data as a function of depth from the surface (through sputtering), standardless quantification has remained a significant challenge due to matrix effects and the complex physics of secondary ion generation. Here, we demonstrate the first successful implementation of the Full Spectrum Method (FSM) for quantitative concentration depth profiling of inorganic thin films using ToF-SIMS. The FSM approach—though documented in only six publications over two decades—effectively minimizes matrix dependencies by leveraging large ion clusters that incorporate numerous neutral atoms, thereby decreasing the ratio of charged particles per cluster. In this study, we systematically quantified molybdenum, sulfur, and oxygen concentrations in physical vapor deposited MoS_2 thin films with varying stoichiometries. Our ToF-SIMS measurements achieved excellent agreement with complementary Rutherford Backscattering Spectrometry performed on reference samples from identical deposition batches. This validation not only establishes FSM as a viable pathway for standardless,

semi-quantitative ToF-SIMS analysis of complex inorganic systems, but also enhances the analytical capabilities of ToF-SIMS for characterizing complex organic specimens, layered structures, and heterogeneous thin films central to emerging technologies in electronics, energy storage, and catalysis.

AS-ThP-6 Insights Into Battery Chemistry Using TOF-SIMS, XPS, and AES*, **Jacob Schmidt**, Sarah Zaccarine, Amy Ferryman,* Physical Electronics USA

Battery devices are complex, multi-layered systems with many surfaces and interfaces that contribute directly to performance. Increased global energy demands and environmental concerns have driven the need for next-generation battery materials with excellent performance and stability, low cost, and improved safety. But the multi-component interfaces and dynamic nature of these systems leads to challenges with their characterization. Developing new materials and technologies to meet energy storage needs requires physicochemical characterization approaches with high-spatial resolution, chemical and morphological information, and correlation of properties.

Time-of-flight secondary ion mass spectrometry (TOF-SIMS), X-ray photoelectron spectroscopy (XPS), and Auger electron spectroscopy (AES) are complementary techniques that, when utilized together, can provide a holistic understanding of complex systems such as batteries. TOF-SIMS offers ppm-level insight into molecular bonding and structural composition, and allows for a wide variety of samples, both in composition (organic or inorganic) and in format (powders, thin films, electrodes). AES provides high-spatial-resolution spectra, images, and maps for nm-range analysis of defects and small sample features. XPS and hard X-ray XPS (HAXPES) can be used to obtain short-range chemical state information. Additionally, these multi-technique instruments have features beneficial to battery device analysis including air-free handling via an inert environment transfer vessel; co-located images, and in-situ/operando analysis of chemical changes as they occur. By using these complimentary techniques, the mass spectra, elemental and chemical-state maps, sputter depth profiles, and electronic structures can all be determined. This poster will highlight these powerful combined capabilities on a range of battery materials that can be used to drive next-generation stability and performance.

AS-ThP-7 Update on New Guides and Tools to Encourage and Facilitate Generation and Reporting of Reliable and Reproducible Information Using Surface Analysis Methods*, **Don Baer**, Lyndi Strange,* Pacific Northwest National Laboratory

A review of recent literature has revealed several common flaws and limitations in surface analysis using various methods, particularly XPS, as well as a notable deficiency in reporting critical sample, instrument, and analysis parameters essential for assessment of the reported information by readers and any efforts to replicate the results. The core assumption is that new and casual method users want to do quality research, but with the increasing number of techniques involved in many research activities, it is a challenge to have expertise for each method. Multiple efforts have been made in response to the identified problems, each intended to provide easily accessible and useful information and tools that can assist an analyst in avoiding the limitations and faulty analyses found in the literature. This poster will provide updated information on some of these efforts. Topics to be addressed include: 1) as a reviewer or reader, you do not need to be an XPS expert to recognize many peak fitting and analysis issues in XPS, 2) an overview of topics addressed in the topical paper collections Reproducibility Challenges and Solutions I and II appearing in the Journal of Vacuum Science and Technology A, 3) an overview of the topics discussed in the shorter Notes and Insights papers now appearing in Surface and Interface Analysis, 4) information about a series of detailed instrument papers starting to appear in Surface Science Spectra to help with instrument parameter reporting and providing descriptions of instrument operation modes, 5) overview of two new ISO standards for reporting on the selection, handling, storage and preparation of samples for surface analysis to be recorded and included as part of sample provenance information, and 6) other journal and web-based papers and platforms intended to assist peak fitting, parameter reporting and error identification.

AS-ThP-8 XPS Analysis of Plasma Exposed TiB2 and ZrB2 Substrates*, **Harry Meyer**,* 1 Bethel Valley Rd, Building 4100*; Lauren Nuckols, Chad Parrish, Juergen Rapp,* Oak Ridge National Laboratory

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-9 Investigation of Desorbed Surface Species Using Atom Probe Tomography*, **Ty J. Prosa**, David J. Larson, David A. Reinhard,* CAMECA Instruments Inc.

Atom probe tomography (APT) utilizes the physics of field evaporation to collect time-of-flight mass spectra from materials [1]. Field evaporation is initiated by either pulsing the electric field (voltage pulse, VP mode) or the specimen temperature via a pico-second laser pulse (LP mode). Fundamental field evaporation characteristics of model materials (mainly metals) have been studied and reported over the years [2], but few recent studies have attempted to expand understanding using modern instrumentation.

Voltage-plus-laser pulsing (VpL) is a new LEAP® 6000 pulsing mode, capable of initiating field evaporation using a simultaneous combination of field and temperature pulses [3,4]. VpL mode lowers the standing field on the specimen surface between pulses, resulting in a reduction of out-of-time evaporation events. The relative timing of the pulses can also be adjusted to terminate delayed evaporation events emitted during the apex cooling process in laser pulse mode (reduction of thermal tails in the mass spectrum). In this study, VpL mode is used to expand the available combinations of standing field, evaporation field, and apex temperature to better understand the full ion emission properties from a standard specimen.

In this poster presentation, we will discuss the experimental and analytical methods that enable exploration of residual gas emission and complex molecule formation trends as a function of evaporation rate, apex temperature, standing field, and evaporation field via VpL mode.

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3. R. Ulfig et al., *Microscopy and Microanalysis* **28** (2022), p. 3190.

4. D.J. Larson et al., *Microscopy and Microanalysis* **28** (2022), p. 718.

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