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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[2] M K Passarelli et al., The 3D OrbiSIMS-label-free metabolic imaging with subcellular lateral resolution and high mass-resolving power, Nature Methods, 2017. 14 (12): p. 1175

[3]J. Zhang et al., Cryo-OrbiSIMS for 3D molecular imaging of a bacterial biofilm in its native state”, Anal. Chem. 2020, 92, 13, 9008–9015.

[4]C. L. Newell et al, Cryogenic OrbiSIMS Localizes Semi-Volatile Molecules in Biological Tissues, Angewandte Chemie Int. 2020, 59 (41), 18194-18200

[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.

[6]F Zani et al., The dietary sweetener sucralose is a negative modulator of T cell-mediated responses. Nature, 2023. 615 (7953): p. 705-711.

[7]PCT/GB2024/050690 - Improved Spectrometer or Imaging Assembly (2024).

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.

[1] P.K. Chu, Materials Chemistry and Physics, 38(3) (1994) 203

[2] A. Franquet et al., Vacuum 202 (2022) 111182

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[1] **ASSD Peter Sherwood Award**

Wednesday Morning, September 24, 2025

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.

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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.

Electronic Materials and Photonics
Room 207 A W - Session EM1+AP+CA+CPS+MS+TF-WeM

Advances in Wide Bandgap Materials and Devices

Moderators: Rachael Myers-Ward, U.S. Naval Research Laboratory, **Chris Richardson**, Laboratory for Physical Sciences

8:00am **EM1+AP+CA+CPS+MS+TF-WeM-1 Progress in Wide and Ultra-Wide Bandgap Semiconductors – Energy Implications***, **John Muth**,* North Carolina State University **INVITED**

The progress in developing wide bandgap semiconductors from idea to commercial products over the past 30 years is one of the great successes of interdisciplinary research between materials, science, physics and electrical engineering. Presently, we are experiencing another step change in the performance of semiconductor devices as ultra-wide bandgap materials (Diamond, Aluminum Nitride, Gallium Oxide) overcome fundamental issues like wafer size, the ability to control conductivity with doping in controlled ways and techniques like wafer bonding become more widely used and high voltage device demonstrations are being made. Similarly, SiC and Gallium Nitride wide bandgap devices are leveraging more mature fabrication technologies including deep ion implantation, sophisticated etching techniques, and high k dielectrics to enable non-planar device geometries, that lower the on resistances and provide increased breakdown voltages. The use of emerging alloys like AlScN offer higher performance higher frequency transistors as well as an addition route to integrate ferroelectric materials with CMOS. Innovations in photonic devices should not be left out with microLEDs for displays and chip to chip communications and increased ability to make low loss visible photonic integrated circuits as well as narrow linewidth lasers for quantum. The goal of this presentation will be to put these advances into context comparing the advances in the different materials and their potential for energy savings for a variety of systems including Artificial Intelligence, Data Centers, and computing and systems where size, weight, power efficiency and reliability matter including ships, planes and satellites.

8:30am **EM1+AP+CA+CPS+MS+TF-WeM-3 Limitations and Effects of Heavy Metal Doping in GaN***, J. Pierce Fix,* Montana State University*; Kevin Vallejo,* Idaho National Laboratory*; Nicholas Borys,* Montana State University*; **Brelon May**,* Idaho National Laboratory

The doping of third-party elements is the backbone of the microelectronics industry, as it allows delicate control of electron/hole concentration, but it can also be used to imbue a host matrix with unique magnetic or optical properties. Wurtzite gallium nitride is a widely studied large bandgap semiconductor. There are reports of doping GaN with numerous elements, with some being extensively employed in commercial applications. However, there are still a few elements which remain completely unexplored. This work investigates the doping limits and effects of select transition metals, lanthanoids, and actinoids in GaN. The structural, electronic, and optical properties of these first-of-a-kind combinations are presented. Embedding single crystal wide bandgap materials with additional functionality will provide building blocks for new multifunctional hybrid systems for novel sensors, quantum science, or meta-multiferroics. Leveraging the non-centrosymmetric piezoelectric host matrix and atomic-level control of dopant species could allow for active tuning of proximity and correlated phenomena, potentially opening the door for applications of actinide elements beyond nuclear fuels.

8:45am **EM1+AP+CA+CPS+MS+TF-WeM-4 Using Raman Spectroscopy to Characterize Stress and Strain in SiC**, ***Michelle Sestak***, HORIBA

Raman spectroscopy is a useful, non-destructive tool for measuring stress and strain in materials like silicon carbide (SiC). In this study, we use Raman spectroscopy to analyze stress and strain in three types of SiC samples: as-cut, diamond-lapped, and after chemical mechanical polishing (CMP). By examining shifts in the Raman peak positions, we identify differences in residual stress caused by each processing step. The as-cut samples show high stress due to mechanical damage, while diamond-lapped samples show partial stress relief. The CMP-treated samples exhibit the lowest stress levels, indicating effective surface relaxation. These results demonstrate how Raman spectroscopy can be used to monitor and compare the effects of different surface preparation techniques on stress in SiC materials.

9:00am **EM1+AP+CA+CPS+MS+TF-WeM-5 Nanoscale GaN Vacuum Electron Devices**, ***George Wang***, *Keshab Sapkota, Huu Nguyen, Gyorgy Vizkelethy,* Sandia National Laboratories

On-chip vacuum electron devices that operate by cold field emission have the potential to combine advantages of traditional vacuum electron devices (e.g. vacuum tubes), such as robustness in harsh environments and high frequency operation, together with those of modern solid-state devices, such as size and energy efficiency. By shrinking the vacuum or "air" channel to nanoscale dimensions well below the electron mean free path in air, such devices can operate at ambient pressures while maintaining the physical advantages of ballistic vacuum transport. Here, we present lateral gallium nitride (GaN) semiconductor nanogap field emission diodes and transistors that exhibit ultra-low turn-on voltage, high field-emission current, and that operate in air. The fabrication of these nanoscale devices is enabled by a two-step top-down etching approach allowing for the necessary sidewall verticality and surface smoothness. We present experimental and modeling results on the field emission characteristics of these devices at various nanogap sizes and operating pressures. Initial results showing the potential of these devices for radiation-hardened, photodetection and high-temperature applications will be presented. These results provide critical new insights into the behavior of this new class of devices and point to future challenges and opportunities. *Sandia National Laboratories is managed and operated by NTESS under DOE NNSA contract DE-NA0003525*

9:15am **EM1+AP+CA+CPS+MS+TF-WeM-6 Combining CVD of Graphene and SiC for Efficient Layer Transfer**, ***Daniel Pennachio***, *Jenifer Hajzus, Rachael Myers-Ward,* US Naval Research Laboratory

Remote epitaxy (RE) is a thin film growth technique that incorporates a release layer into the material stack, allowing for transfer of the deposited material with minimal defects [1]. Transferred 2D two-dimensional (2D) material, such as graphene, is commonly used for a release layer, but the transfer step can degrade the film and increase process complexity. To avoid this, we examine *in situ* graphitic carbon growth on SiC substrates before subsequent SiC epitaxy in the same chemical vapor deposition (CVD) RE process. RE SiC and subsequent SiC epilayer transfer is desired since isolated SiC membranes are excellent for quantum photonics and SiC substrate reuse can provide significant cost savings. Despite these benefits, the high-temperature hydrogen-containing CVD environment can damage graphene, making RE difficult under standard SiC growth conditions [2].

This study established growth windows for *in situ* graphene via propane-based hot wall CVD. This propane-based graphene growth enables an efficient transition to subsequent SiC deposition using established SiC growth conditions since it shares a similar hydrogen ambient to standard SiC CVD. Growing at 1620 °C in 20 slm H_2 with 20 sccm propane flow produced predominantly monolayer (ML) graphene films on on-axis 6H-SiC(0001) substrates with minimal defects found in Raman spectral maps. Films grown on 4° off-axis 4H-SiC(0001) substrates were multilayer (6 ML) graphitic carbon despite experiencing the same conditions as the on-axis substrates. This optimized graphene growth condition was used for subsequent RE attempts to study the effect of SiC precursor dose, C/Si ratio, and growth rate on epilayer crystallinity and graphene barrier damage. SiC crystalline quality appeared correlated to growth rate, with lower growth rates producing smoother films with fewer polytype inclusions. Single-crystalline, polytype-pure SiC epilayers was achieved on 4° off-axis CVD graphene/4H-SiC(0001). Effects of initial SiC growth parameters on the graphitic carbon release layer were explored via cross-sectional transmission electron microscopy (TEM) and attempts at epilayer transfer. Some growth interfaces exhibited non-uniform multilayer graphitic carbon, motivating further study of this growth system to improve boundary uniformity and SiC epilayer quality.

[1] Kim, Y., Cruz, S., Lee, K. et al. Nature 544, 340–343 (2017).

[2] Pennachio, D. J., Hajzus, J. R., & Myers-Ward, R. L. JVST B, 43(2). (2025).

9:30am **EM1+AP+CA+CPS+MS+TF-WeM-7 Multiscale Modeling of Self-heating Effects in AlGaN/GaN High Electron Mobility Transistors (HEMT)**, ***Jerry Comanescu***, National Institute of Standards and Technology*; Albert Davydov,* NIST-Gaithersburg*; Michael Shur,* Theiss Research, Inc.*; Tyler Gervasio, Behrang Hamadani, Michael Lloyd,* NIST-Gaithersburg

AlGaN/GaN based High Electron Mobility Transistors have emerged as state-of-the-art devices in power and RF electronics because of the outstanding electronic properties of the AlGaN/GaN heterostructure. The large breakdown field of GaN (3.3 MV/cm, 11 times higher than silicon) enables HEMT operation in the kV-range while the high mobility of the two-dimensional electron gas at the AlGaN/GaN interface ensures that HEMTs have a very low on-resistance. In addition, the wide bandgap of GaN makes HEMT devices particularly suitable for high-temperature, high-power, and high-current operations. However, unlike silicon-based devices, the performance of current GaN based devices falls significantly shorter than what is expected based on the outstanding properties of GaN material. This gap in performance is even larger when HEMT devices experience self-heating under high-power operation regime, which strongly affects the device lifetime and reliability. Therefore, understanding the high-temperature operation and the self-heating effect is critical for improving the device design. We report on self-heating effect in AlGaN/GaN HEMTs. We interpret our measurement results using a new compact CAD self-heating model. The model is based on the Unified Charge Control Model (UCCM) and is in excellent agreement with the measured data. Our results allow for the identification of the material properties and device parameters primarily responsible for the temperature dependencies of the device characteristics. The measured temperature dependencies also reveal non-ideal effects related to charge trapping, including threshold voltage instability and current-voltage characteristic hysteresis. The model accounts for the temperature distribution inside the HEMT devices (e.g., distribution of temperature along the channel) which are evaluated by a combination of TCAD simulations, heat transfer finite element simulations, and experiments performed on commercial HEMT devices. The developed compact self-heating model augments TCAD simulations for the Device Technology Co-Optimization approach by linking the AlGaN/GaN HEMT performance and design optimization to material and interface properties.

9:45am **EM1+AP+CA+CPS+MS+TF-WeM-8 Atomic Layer Deposition of High-k Oxide Layers on Aluminum Gallium Nitride: Insight from Time-Resolved Synchrotron Studies**, *Nishant Patel, Shreemoyee Chakraborty,* Lund University, Sweden*; Byeongchan So,* lund University, Sweden*; Minho Kim, Alexis Papamichail,* Linkoping University, Sweden*; Rosemary Jones,* Max IV Laboratory, Sweden*; Erik Lind, Vanya Darakchieva,* ***Rainer Timm***, Lund University, Sweden

Gallium nitride (GaN) and aluminum gallium nitride (AlGaN) are the materials of choice for enabling power electronic devices with superior energy efficiency and very high switching frequency. Such devices are based on metal-oxide-semiconductor (MOS) stacks, where downscaling and leakage control require gate insulators with high dielectric constant, so-called high-k oxides, such as HfO_2. However, device performance and especially switching frequencies are often limited by the low quality of the (Al)GaN/high-k interface. Atomic layer deposition (ALD) is typically used for the synthesis of ultrathin, conformal high-k layers, where the choice of oxide material, ALD parameters, and pre-ALD cleaning methods strongly influence film and interface quality. Many important details about the physics and chemistry of the interface formation still remain unknown. Furthermore, until now all efforts to explore the high-k oxide film formation are based on *ex situ* approaches, meaning that film deposition and characterization of the resulting interface occur in separate steps.

Here, we will present a first time-resolved investigation of the ALD reactions of HfO_2 on (Al)GaN. We have used synchrotron-based ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) and implemented the ALD process in the AP-XPS setup at the MAX IV synchrotron facility. Thus, we succeeded in mapping surface chemistry and electronic properties *in situ* during subsequent ALD half-cycles, which consisted of the deposition of tetrakisdimethylamido-hafnium (TDMA-Hf) and water. We observed a rather inefficient first ALD cycle, compared to other semiconductor ALD reactions, which improved with increasing aluminum content. Thickness and chemical composition of the resulting Hf-oxide film varied significantly if the order of the precursors was changed (TDMA-Hf first or water first). Both observations are against the established ligand-exchange ALD model and highlight the importance of in-depth studies for improving the quality of high-k layers on (Al)GaN.

In addition, we have used XPS to systematically investigate the electronic properties and chemical composition of the interface between different (Al)GaN substrates and HfO_2 or Al_2O_3 high-k oxide films, for different ALD temperatures, where Al_2O_3 layers typically resulted in a more stoichiometric oxide film. The choice of pre-ALD cleaning methods was also found to be of importance, which can enhance ALD efficiency but also result in significant interface contamination. We will discuss how our structural results can be easily implemented to improve device performance.

Electronic Materials and Photonics
Room 207 A W - Session EM2+CA+CPS+MS+SE+TF-WeM

Processing Ultra-Wide Band Gap Ga_2O_3

Moderators: Daniel Pennachio, Naval Research Laboratory, **Virginia Wheeler**, U.S. Naval Research Laboratory

11:00am **EM2+CA+CPS+MS+SE+TF-WeM-13 Ga_2O_3 Polymorphs: Epitaxial Film Growth, Characterization and Contacts***, **Lisa Porter**, Jingyu Tang, Kunyao Jiang, Robert Davis, Posen Tseng, Rachel Kurchin,* Carnegie Mellon University*; Luke Lyle,* Penn State Applied Research Labs*; Carlo Schettini Mejia,* Carnegie Mellon University **INVITED**

The last decade has shown a dramatic increase in research on gallium oxide (Ga_2O_3) as an ultra-wide bandgap semiconductor for electronics that can operate in extreme conditions, such as high power, high temperature and radiation exposure. This presentation will focus on unique and intriguing characteristics associated with two processes that are necessary to produce Ga_2O_3-based devices: the growth of epitaxial films and the formation of ohmic and Schottky contacts. Whereas β-Ga_2O_3 is the thermodynamically stable phase, the other, metastable, phases of Ga_2O_3 can be produced as epitaxial films in either mixed-phase or pure-phase form. Our results, along with those in the literature, indicate that the phase content and other film properties strongly depend on the growth method (e.g., MOCVD, HVPE, mist CVD, etc.) and other conditions during film growth, such as precursor chemistry, flow rates, temperature, and substrate material / orientation. Our group has also conducted comprehensive studies of ohmic and Schottky contacts to β-Ga_2O_3. For reasons that are not well understood, only a few metals have been demonstrated as practical ohmic contacts to Ga_2O_3. Whereas Ti/Au contacts annealed at 400–500 °C are widely used, Cr/Au contacts annealed in a comparable temperature range also form ohmic contacts to Ga_2O_3. Controlled studies of several different elemental-metal Schottky contacts show that their electrical behavior highly depends on the particular Ga_2O_3 surface on which they're deposited; observed behavior ranges from Fermi-level pinning on the (-201) surface to near-ideal Schottky-Mott behavior on the (100) surface. Examples of the phenomena outlined above will be summarized and presented using results from high-resolution transmission electron microscopy, x-ray diffraction, and electrical measurements.

11:30am **EM2+CA+CPS+MS+SE+TF-WeM-15 Compensating Interfacial Parasitic Si Channels in β-Ga2O3 Thin Films Via Fe δ-doping***, **Prescott Evans**, Brenton Noesges, Jian Li, Mark Gordon, Daram Ramdin, Shin Mou, Adam Neal, Thaddeus Asel,* Air Force Research Laboratory, USA

β-Ga_2O_3 is a promising material for high power applications given an ultra-wide bandgap and predicted high break down field. One challenge with β-Ga_2O_3 for lateral device architectures is the presence of undesired Si between epitaxial thin film and substrate which creates a parasitic conduction channel. This channel limits performance and can prevent device modulation. Attempts to remove this interfacial layer using etch methods have proven mostly successful. However, in plasma-assisted oxide molecular beam epitaxy (PAMBE), conventional removal efforts appear unsuccessful. Our results show interfacial Si can reaccumulate at clean β-Ga_2O_3 surfaces from various Si sources inside the MBE tool such as the Si doping effusion cell. Hence, careful growth steps must be considered to avoid Si reaccumulating onto clean β-Ga_2O_3 surfaces in PAMBE. This work presents an alternative to mitigate the influence of this Si parasitic conduction channel via Fe delta doping at the interface. We demonstrate how a thin Fe layer at the interface can compensate interfacial Si and create an interface without excess free charge. The growth methodology presented involves multiple steps to avoid Fe diffusion from the interface. We first deposit the Fe followed by a low temperature (LT) undoped buffer before depositing an Si doped channel layer at higher deposition temperatures. The LT buffer helps minimize Fe surface riding and diffusion while the increased substrate temperature during the Si doped channel improves surface roughness. Secondary ion mass spectrometry (SIMS) results show Fe only resides at the interface between substrate and LT buffer layer with Fe concentration in the LT buffer and Si doped channel below the noise floor of the instrument. Furthermore, SIMS shows a smooth transition in Si concentration from the LT buffer into the intentionally Si-doped channel region avoiding any spikes between the two layers, indicating high degree of controlled doping localization. Initial capacitance-voltage (C-V) measurements on samples with the Fe compensation show no spike in carrier concentration near the substrate interface indicating Fe is fully compensating interfacial Si. These results demonstrate a potential method to mitigate parasitic Si conduction channels in β-Ga_2O_3. However, time-dependent C-V results show there is some capacitance transients when the sample is fully depleted. While Fe seems initially promising other compensating acceptors such as N or Mg need to be explored given this observation of capacitance transients in Fe-doped structures. Overall mitigating this parasitic interface will help improve yield and performance uniformity in fabricated devices.

11:45am **EM2+CA+CPS+MS+SE+TF-WeM-16 Investigating Metal Gate-Driven Interfacial Reactions in ALD-Grown Al_2O_3 on β-Ga_2O_3***, **Joy Roy**, Adam A. Gruszecki,* The University of Texas at Dallas*; Khushabu S. Agarwal, Paolo La Torraca, Karim Cherkaoui, Paul K. Hurley,* Tyndall National Institute, University College Cork, Ireland*; Chadwin D. Young, Robert M. Wallace,* University of Texas at Dallas

β-Ga_2O_3 is a leading candidate semiconductor for next generation power electronics with the potential to outperform GaN and SiC owing to its high breakdown strength paired with low power losses.[1] Integrating a robust gate dielectric and stable oxide interface is critical in leveraging these properties of β-Ga_2O_3.[2] However, this cannot be achieved without also considering the gate electrodes' reactivity and their influence on oxide properties. This work explores interfacial reactions—particularly those associated with oxygen scavenging—and the resulting variations in gate oxide performance induced by Ni and Ti gate metals in Al_2O_3 on bulk (001) β-Ga_2O_3 substrates.

Interface reactions were analyzed via *in situ* X-ray photoelectron spectroscopy (XPS) in an ultrahigh vacuum (UHV) cluster system. β-Ga_2O_3 samples were scanned as-loaded, after atomic layer deposition (ALD) of ~2 nm Al_2O_3, and a third time following UHV electron beam deposition of Ni or Ti (~1 nm) to assess changes in interface chemistries. Additional chemical states in Ga_2O_3 were below the XPS detection limit after oxide and metal deposition. However, an AlO_x (sub stoichiometric) state appeared in Al core levels (2*p* or 2*s*) after introducing Ti. This, along with a TiO_x state in Ti 2*p*, may imply oxygen scavenging from Al_2O_3. While both metals reacted with surface organic residues from metal-organic precursors, Ti exhibits more carbide formation at the gate/dielectric interface. Additionally, MOSCAPs were fabricated with ~12 nm Al_2O_3 and 10/100 nm of either Ni/Au or Ti/Au as the gate metal for I-V and C-V characterization. Ni/Au devices showed lower frequency dispersion and over two orders of magnitude lower gate leakage in accumulation than Ti/Au samples, consistent with the XPS findings. Dielectric breakdown strength will be further studied to explore electrical stability of the oxides.

In conclusion, a fundamental understanding of gate metals' influence on interface properties is essential for precisely predicting device behavior in power electronics.

This work was supported by the National Science Foundation (Grant ECCS 2154535) at the University of Texas at Dallas and by Research Ireland (Grant 12/US/3755) at Tyndall National Institute through the US-Ireland R&D Partnership. (Corresponding author: Robert M. Wallace.)

[1] S. J. Pearton, F. Ren, M. Tadjer, and J. Kim. J. Appl. Phys. **124**, 220901 (2018).

[2] C. V. Prasad, and Y.S. Rim, Mater. Today Phys. **27**, 100777 (2022).

Chemical Analysis and Imaging at Interfaces
Room 205 ABCD W - Session CA-WeA

Advances in Experimental and Theoretical Insights Into Material Interfaces

Moderators: Jiyoung Son, Oak Ridge National Laboratory, **Samuel Tenney**, Brookhaven National Laboratory

2:15pm **CA-WeA-1 Optimizing in situ liquid ToF-SIMS using SALVI and IONTOF M5-NCS***, **Jiyuong Son**, Anton Levlev, Jacob Shusterman, Xiao-Ying Yu,* Oak Ridge Natinal Laboratory

In situ time-of-flight secondary ion mass spectroscopy (ToF-SIMS) was enabled to study liquids using a vacuum compatible microfluidics device. This approach has brought a wider range of sample analysis capabilities in vacuum instrumentation, specifically applications in interfaces involving the condense liquid phase. The successful operation of in situ ToF-SIMS also has been presented previously using an IONTOF V instrument. We establish in situ liquid ToF-SIMS using the IONTOF MS-NCS instrument at the Oak Ridge National Laboratory (ORNL). Several parameters in the instrument setting (i.e., Primary beam current, voltage, pulse mode) were modified to optimize signal intensity and obtain more effective data collection in a wide mass range. A systematic study was performed including LMIG aperture, tip material of primary gun, primary beam current, voltage, and microfluidic device condition. If just following the procedure for the IONTOF V instrument, in situ liquid SIMS data suffered from low secondary ion intensity and only a narrow mass range was available for spectral and image collection. To acquire higher secondary ion counts, one procedure is not possible to “fit for all” for different ToF-SIMS instruments. In this work, we will present findings of in situ liquid ToF-SIMS optimization using the IONTOF M50NCS platform located in the center for nanophase materials science (CNMS) at ORNL. We demonstrated higher mass resolution in liquid SIMS spectral acquisition using the LIMG buncher voltage mode. Higher total secondary ion counts per sec (~40k ions / sec) with altering single pulse width of the LMIG primary beam was also achieved. The optimized in situ liquid SIMS procedure will be used to study complex interface chemistry in the future.

2:30pm **CA-WeA-2 First Principles-Based Defect Engineering to Enhance Layered Ni-rich Cathode Performance***, **Sumaiyatul Ahsan**, Faisal M. Alamgir,* Georgia Institute of Technology, USA

We present a strategy to enhance the capacity retention of Ni-rich cathodes by modifying the electronic structure via an oxygen-vacant surface layer. Rather than addressing external factors that result in surface coatings for protection against electrolytic attack, we emphasize that intrinsic issues with electronic structure can also contribute to degradation, making materials more vulnerable in the first place. Our DFT calculations show that introducing oxygen vacancies (OV) in $LiNiO_2$ stabilizes reactive Ni^{2+} ions and reduces the overlap between O2p and Ni3d orbitals. To validate our predictions, we examined NMC811 ($LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$), known for its high initial capacity but tendency for capacity loss. An in-situ annealing XRD reveals the optimal temperature range for surface OV formation while retaining the layered bulk structure. Then, a one-step thermal treatment was employed to create a core-shell structure with 6.9% surface OV, resulting in a 9.4% improvement in capacity retention over 100 cycles at 1C compared to the unmodified sample. Scanning Transmission Electron Microscopy (STEM) visualized the vacancies and edge defects, and we implemented a quality control framework using XPS, tabletop XRD, and lab-scale h-XAS for efficient measurement of cation disorder, OV concentration, and bulk homogeneity. Our study on LNO and NMC811 demonstrates that employing OV to tune the electronic structure provides a universal solution for capacity fading in Ni-rich cathodes.

2:45pm **CA-WeA-3 Extending Ambient Pressure X-Ray Photoelectron Spectroscopy to Plasma Studies: A Custom-Built Plasma Source Apparatus***, **Jun Cai**, Yang Gu,* Shanghaitech University, China*; Yong Han,* shanghaitech University, China*; Hui Zhang,* Shanghai Synchrotron Radiation Facility, China*; Zhi Liu,* Shanghaitech University, China

The characterization of the electronic structure and chemical states at heterogeneous interfaces (e.g., gas-solid or liquid-solid) can be effectively achieved using ambient pressure X-ray photoelectron spectroscopy (AP-XPS). However,acquiringthese properties under plasma conditions remains significant challenges. In this study, we introduce an AP-XPS system equipped with acustom-builtspatially confinedplasma source. This configuration confines the plasma to a controlled region, with the plasma intensity precisely regulated by adjusting either the working distance or the applied voltage. This system enables the direct detection of plasma electronsand real-time characterization of the surface states during plasma-surface interactions. To validate its efficacy and versatility, we conducted two proof-of-concept experiments: argon (Ar) plasma etching of graphene and oxygen plasma oxidation of platinum (Pt). The results demonstrate that Ar plasma effectively etches graphene, as evidenced by the distinct changes in the XPS spectra. Similarly, exposure of Pt surface to oxygen plasma induces pronounced surface oxidation. Thissystem significantly extends the operando capabilities of AP-XPS forin situ studies of plasma-enhanced reactions.Its application holds considerable promise for advancing fundamental and applied research in materials science and chemical engineering, particularly in the areas of surface modification and catalytic processes.

3:00pm **CA-WeA-4 Infrared Nanoscopy of Electron-Beam Modified Metal Organic Frameworks***, **Samuel Tenney**,* Brookhaven National Laboratory*; Andrea Kraetz,* Johns Hopkins University*; Prerna Prerna, Ilja Siepmann,* University of Minnesota*; Michael Tsapatsis,* Johns Hopkins University

Metal organic frameworks (MOFs) are a class of porous materials that are promising for applications in many areas including gas separations and sorptions. Some MOFs, such as ZIF-L, can be chemically modified by exposure to an electron-beam to tailor their properties. This chemical modification by electron-beam exposure is known to modify their solubility among other properties. The modified MOFs have been characterized with nanoscale infrared techniques, namely photothermal infrared (PTIR) or AFM-IR and optical-photothermal infrared (O-PTIR), to understand the chemical changes that happen and the possible application of these materials towards gas separation. The results show a two-step process in the chemical modification of the MOFs with increasing electron-beam exposure.

3:15pm **CA-WeA-5 Probing the Electronic-Ionic-Mechanical Coupling at Solid-Electrolyte/Electrode Interfaces***, **Yue Qi**,* Brown University **INVITED**

Electrochemical interfaces are critical components of energy conversion and storage devices. In solid-state batteries, the electrode/electrolyte interfaces must enable fast charge transfer reactions while maintaining physical contact throughout cycling. To probe the highly coupled electrochemical, mechanical, and physical responses and their evolution at these interfaces, multiscale modeling and multimodal characterization must work hand in hand.

At well-contacted interfaces, we draw an analogy to electron transport at metal/semiconductor interfaces and develop a density functional theory (DFT)-informed band-alignment model for intrinsic ionic resistance. This model incorporates DFT-computed electronic and point defect properties of the contacting phases to predict space-charge layer formation, potential drop, and electrostatic dipole at the electrode/solid-electrolyte interface. It is essential for interpreting *in operando* Kelvin probe force microscopy (KPFM) measurements of local potential profiles across interfaces of solid-state batteries—especially considering the dependence on lithium concentration and applied electric potential. To further probe band bending at buried interfaces, depth-resolved cathodoluminescence spectroscopy (DRCLS) is being developed to enable non-destructive characterizations.

Extrinsic interface resistance arises from changes in the contact area, which naturally decreases during Li stripping at Li/solid electrolyte interfaces. To capture the governing mechanisms across multiple length and time scales—including interface interactions, vacancy hopping, and plastic deformation, we integrated DFT simulations, kinetic Monte Carlo (KMC) methods, and continuum finite element modeling (FEM). By assuming the self-affine nature of multiscale contacts, we predicted the steady-state contact area as a function of stripping current density, interface wettability, and stack pressure. These predictions are supported by high-spatial-resolution operando scanning electron microscopy.

Together, these modeling advances are being integrated into a comprehensive framework to guide the design and development of next-generation all-solid-state batteries and electrochemical random-access memory (ECRAM) devices.

Chemical Analysis and Imaging at Interfaces
Room Ballroom BC - Session CA-ThP

Chemical Analysis and Imaging at Interfaces Poster Session

CA-ThP-1 Depth Profiling of Perovskite Tandem Solar Cells Using Small Ar Gcib in Cluster Sims at Cryogenic Temperatures*, **Kate McHardy**, Naoko Sano,* Ionoptika Ltd., UK

Many Secondary Ion Mass Spectrometry (SIMS) instumentscan perform at cryogenic temperatures, however, complex sample handling requirements and high cryogen consumption have meant that such experiments have hitherto been expensive and complicated. Utilising Ionoptika's J Series III cluster SIMS instrument with Cryo stage, we show that long-term Cryogenic studies may be carried out on both soft and hard materials, with demonstrable improvements in results compared to RT analysis. We demonstrate 3D depth profiling of perovskite solar cells and show that the precision of the depth profile is increased at Cryo temperatures when compared with RT analysis. The current common approach to analyse such samples is to peel off the hardest capping layer and then analyse the perovskite layers using Ar GCIB to sputter and Bi to analyse. Alternatively, a Cs beam may be used to sputter to just above the interface, and then low energy an Ar GCIB and Bi beam used for sputtering and analysis. However these approaches are flawed; the peeling process can cause migration of elements to the free surface, and Cs and monoatomic Ar sputtering can cause intermixing of consecutive layers.The J Series III Cluster SIMS system employs GCIB as the primary ion beam which can sputter and analyse simultaneously, meaning no sputter-only cycles. For thin layers, this is crucial, asit precludes loss of information about the layers and/or interface. In addition, the GCIB used has a high (70 kV) beam energy and provides a range of cluster sizes from monoatomic to large cluster sizes such as 30k. We have previously demonstrated use ofsmaller cluster beams to sputter though 1.5 um thickness of perovskite solar cell samples from the capping layer to the glass substrate with less preferential sputtering and intermixing effects. Therefore, J Series III analysis using a small cluster GCIB promises to show more 'genuine' information than the current dual beam method for hard and mixed materials including metals and organics.In this work, pristine and aged samples of perovskite tandem solar cells are analysed with an Ar350 Cluster at 70 keV beam in the J Series III at RT and cryo temperatures to demonstrate the suitability, less intermixing effect and lack of preferential sputtering especially at cryo temperatures that show higher depth resolution and sputter rate with less damage.We conclude that analysis of hybrid semiconductor samples results in superior data when conducted with small clusters at Cryogenic temperatures.

CA-ThP-2 Uncovering Coke-Resistant Two-Dimensional Metal Carbide Catalysts Using ToF-SIMS*, **Tobias Misicko**,* Louisiana Tech University and Oak Ridge National Laboratory*; Gabriel Parker,* Oak Ridge National Laboratory*; Yang Xiao,* Louisiana Tech University*; Xiao-Ying Yu,* Oak Ridge Natinal Laboratory

Catalysts can be described by three important aspects activity, selectivity, and stability. Activity is the ability of a catalyst to convert reactants into products. Selectivity is the ratio of the desired product to the total amount of converted molecules. Stability is the ability of a catalyst to maintain activity with respect to time on stream (TOS, time since initial contact of reactant gas to the catalyst bed) in continuous reactors. MXene, a class of two-dimensional metal carbides, can be used as a support material to create a coke-resistant nanolayer catalyst with excellent activity, selectivity, and stability. MXene has empirical formula of $M_{n+1}X_nT_x$, where M is an early transition metal, X is a carbon or nitrogen, and T is a surface functional group (such as F^- or OH^-). In our prior studies,[1,2] platinum (Pt) was loaded onto Mo_2TiC_2 MXene using incipient wetness impregnation to synthesize a 0.5% (wt.) Pt/Mo_2TiC_2 Pt nanolayer MXene catalyst. The Pt nanolayer catalyst exhibited excellent activity with turnover frequencies (TOFs, converted molecules per surface Pt atom) of 0.4~1.2 s^{-1} for converting methane[1] and ethane[2]. 0.5% Pt/Mo_2TiC_2 displayed high selectivity, with over 98% to C_2 products for non-oxidative coupling of methane (NOCM) and over 95% selectivity for catalytic dehydrogenation of ethane to ethylene. Robust catalyst stability is obtained with no loss in catalytic activity for 72 hr. and 24 hr. for NOCM and ethane dehydrogenation, respectively, owing to its strong coke-resistance. However, the active site and surface activity are not easy to study. In this presentation, we used time-of-flight secondary ion mass spectrometry (ToF-SIMS) to investigate MXene catalytic effects. ToF-SIMS is a highly sensitive surface analysis technique, capable of molecular, atomic, and isotopic analysis. Depth profiling and mass spectral mapping allow for analysis of subsequent monolayers of the catalyst's surface. Measurements, including surface spectra, two-dimensional imaging, secondary electron imaging, and depth profiling (three-dimensional imaging), were used to probe the surface and reveal structures of both unloaded Mo_2TiC_2 MXene support and 0.5% Pt/Mo_2TiC_2 nanolayer MXene catalysts. The large dispersion of Pt^+ ions throughout the bulk of Pt/Mo_2TiC_2 nanolayer MXene supports the hypothesis that the MXene channel prohibits access to the terrace site, a critical site for the structure-sensitive coking reaction.

[1] Li Z. *et al.*, *Nano Research,* 17 (**2024**) 1251–1258.

[2] Li Z. *et al.*, *Nature Catalysis,* 10 (**2021**) 882–891.

CA-ThP-3 The Origins of Binding Energy Shifts at the Plasma-Exposed Dielectric Samples and in the Gas Phase Measured by Plasma XPS*, J. Trey Diulus,* NIST-Gaithersburg*; Ashley R. Head, Jorge Anibal Boscoboinik,* BNL*;* ***Andrei Kolmakov,*** NIST-Gaithersburg

Modern near-ambient pressure X-ray photoelectron spectroscopy (NAP or AP-XPS) instruments now cover the pressure range typical of standard plasma applications, expanding the capabilities of XPS to plasma environments. We recently demonstrated that XPS spectra can be successfully collected in these conditions, extending the application of XPS to plasma interactions [1]. In previous work [2], we highlighted the influence of plasma chamber wall reactions on sample surface chemistry and showed that plasma-XPS can capture plasma chemistry in the gas phase.

In this study, we apply plasma-XPS to poorly conducting samples, where we observed anomalous XPS binding energy shifts due to sample charging during plasma exposure. We propose mechanisms that explain these shifts. Additionally, we noted plasma-induced binding energy shifts and peak splitting when measuring XPS from the plasma gas phase.

Plasma-induced charging and damage of wafers is a well-known challenge in semiconductor fabrication [3], and plasma-XPS offers significant potential for advancing diagnostics and mitigation strategies for these issues.

References

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CA-ThP-4 Tapping into Charge Storage with Operando-XPS using Coplaner Capacitors and Ionic Liquid Mixetures*, Ezgi Kutbay,* ***Sefik Suzer,*** Bilkent University, Turkey

We use X-Ray Photoelectron Spectroscopy under bias to track surface population and electrical potentials on multilayered graphene electrodes with two ionic liquid mixtures, one containing the same cation (DEME+) and two different anions (TFSI- and BF4-) and the other one with two different cations (DEME+ and Rb+) and same anion (TFSI-). As bias increases, peak intensities change and binding energies shift, revealing both ion concentrations and also the local electrical potentials simultaneously. In addition the capacitance of the device increases significantly, providing crucial insights for developing new energy storage devices.

CA-ThP-6 Meeting the Demand for Surface Sensitivity: The Role of LEIS*,* ***Joshua Pinder,*** Brigham Young University*; Stanislav Prusa,* Central European Institute of Technology, Czechia*; Matthew Linford,* Brigham Young University

Low-Energy Ion Scattering (LEIS) provides unmatched sensitivity to the outermost atomic layers of materials, making it a critical tool for surface analysis. This poster presents a practical guide to LEIS spectral interpretation, featuring spectra from a diverse range of materials. While covering key theoretical aspects, the focus remains on practical insights for researchers who rely on LEIS data, whether through collaboration or literature. Topics include surface peak identification, reionization effects, multiple scattering, contamination impacts, and material-specific spectral features. Spectra from modern high-sensitivity LEIS instruments illustrate both fundamental and advanced phenomena across various materials of technological interest. By clarifying LEIS spectral characteristics and applications, this guide aims to enhance accessibility and understanding within the broader scientific community.

CA-ThP-7 Mass Spectral Molecular Mapping Shows Benefits of Thermal Evaporation in Prelithiated Silicon-Based Composite Electrodes*, **Ivan Matyushov**, Gabriel Parker, Amanda Musgrove, Gabriel Veith, Xiao-Ying Yu,* Oak Ridge National Laboratory

Key words: ToF-SIMS, prelithiation, anode, solid-state lithium-ion battery, lithium silicateSilicon carbon composites have become increasingly popular as potential anodes for solid-state lithium-ion batteries due to their large storage capacity. However, their current application is inhibited by the disruptive volume expansion and continuous solid electrolyte interface (SEI) layer formation that reduces their initial columbic efficiency (ICE). Prelithiation is used to counteract the loss of lithium ion (Li^+) by adding reserved lithium ions to the electrode. Prelithiation via thermal evaporation is a newly developed technique with limited studies on its effectiveness and process variations. Thermal evaporation was done through a 400-steel mesh placed over the electrode which directed the lithium metal deposition and diffusion into ‘islands’ or channels in a set of electrodes. Using this steel mesh resulted in less strain and volumetric expansion in the electrodes. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is used to highlight the benefits of prelithiation via thermal evaporation with a steel mesh in this study. Three ToF-SIMS measurement modes are used to visualize the deposition of lithium into ‘islands’, to identify Li_xSi_y alloy and $Li_xSi_yO_z$ silicate formation, and to display the distribution of lithium throughout the electrodes. The SIMS molecular imaging results validate the formation of the LiSi alloy and $Li_xSi_yO_z$ silicate upon prelithiation. Through depth profiling three-dimensional and surface two-dimensional imaging in SIMS, we confirm that prelithiation by thermal evaporation effectively incorporates lithium into the silicon composite anode as desired. The multimodal mass spectral imaging results help validate the effectiveness of thermal evaporation for prelithiation, particularly in combination with a steel mesh.

CA-ThP-9 Evaluation of Imbedded Barium in Graphite for Nuclear Engineering in ToF-SIMS*, **Gabriel Parker**, Thomas Muth, Victor Bautista, Xiao-Ying Yu,* Oak Ridge National Laboratory, USA

Advanced manufacturing of cermets, heat-resistant materials made of ceramic and sintered metal, is necessary for radio isotope production to decrease waste and increase efficiency. The High Flux Isotope Reactor (HFIR) at the Oak Ridge National Laboratory currently uses Al as the filler material for irradiation targets. While Al has offered the ease of use and high thermal conductivity, it is limited by the post processing procedures creating a high charge density of the Al cation, creating instable aluminum nitrates, and forming oxidation decreasing the overall performance of the irradiation target. Transitioning from Al to a graphite matrix could reduce the issues aluminum poses. Graphite has similar thermal stability, thermal conductivity, and chemical properties. The manufacturing process using carbon can reduce waste by lowering solution volumes and overall complexity. ^{223}Ra is a radio isotope used for cancer treatments and is produced via a series of beta decays starting with ^{226}Ra. To test method development, Ba, is used as a surrogate to radium. This work examines the barium encapsulation by graphite using time-of-flight secondary ion mass spectrometry (ToF-SIMS). Specifically, high resolution spectroscopy and 2D/3D imaging modes were used to study the $BaCO_3$ pellets prepared in different manner.Current manufacturing process uses a mixture of graphite and barium carbonate either vacuum hot pressed or cold pressed and sintered. The mass spectrometry results verify that BaC as this is the preferred extraction radio isotope and not the oxide or carbonate. Also, depth profiling results show the $BaCO_3$, BaC_2, and BaO distributions across the surface and into the bulk of the pellet, indicative of the usefulness of different pellet processing steps.

Key words:

Barium, Radium, Graphite, Advanced Manufacturing, Nuclear Engineering, Radioisotopes, ToF-SIMS

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