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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[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.

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10:30am **AS+BI+CA-MoM-10 ASSD Peter Sherwood Award Talk: In situ Detection of Proteins, Xenobiotics and Metabolomics via OrbiSIMS*, David Scurr*[1]*,*** University of Nottingham, UK **INVITED**

The application of secondary ion mass spectrometry (SIMS) to detect of proteins at surfaces and within tissue has significant potential in healthcare, medicine and medical device development. This approach offers the potential of an *in situ* analysis and does not require digestion and/or matrix application prior to analysis. The analysis of proteins has previously been limited due to fragmentation resulting in only single amino acid secondary ions, devoid of primary structural information. Here we use the OrbiSIMS technique to achieve *in situ* label and matrix-free 3D mapping of undigested proteins at surfaces. We successfully applied de novo sequencing for identification of proteins using fragments generated by the GCIB. We analysed 16 model protein films in a range of sizes from insulin (6 kDa) to fibronectin (272 kDa), achieving amino acid sequence coverages up to 53% [1]. Additionally we assigned highly specific protein ions in a monolayer biochip sample and successfully assigned diagnostic peptide sequences from collagen, keratin and corneodesmosin within the depth profile through human skin [1].

Further analysis of native *ex vivo* human tissue also allowed the elucidation of the chemical landscape of the of the *stratum corneum* including subtle chemical variations within single skin strata and / or individual cells [2]. In addition to the biological analysis enabled using the OrbiSIMS, the relatively high sensitivity and chemical specificity offers the ability to detect the distribution of xenobiotic compounds delivered to skin, namely antibacterial, cosmetic and pharmaceutical agents have also been demonstrated. This includes the detection of xenobiotic chemistries delivered to human skin *in vivo* and *ex vivo* at concentrations <100 ppm [2].

In healthcare applications, the delivery of mRNA-based vaccines against SARS-CoV-2 have been clearly demonstrated in recent years [3]. This research aspires to characterise both delivery of LNPs to cells and provide insights into their metabolic impact using OrbiSIMS. Peaks related to components of the LNP were identified using reference standards and observed to have peak intensities at dosage time 4 hours. Significant changes in biological compounds were investigated to determine metabolic pathways affected using MetaboAnalyst. Over 600 endogenous metabolites have been identified, significant changes in endogenous compounds were identified including fatty acids and small metabolites, correlating with LNP uptake, indicating these mechanisms were impacted by LNP delivery.

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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*[2]*,*** 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

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[1] **ASSD Peter Sherwood Award**

[2] **JVST Highlighted Talk**

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

[3] J. Bennett et al., `Proc. SiGe: Materials, Processing, and Devices,vol. 2004-07, (Honolulu, USA), 239, Electrochemical Soc

11:45am **AS+BI+CA-MoM-15 Evidence of Surface Localization of Hydrogen and Zirconium Hydride in Zircaloy with Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS)**, ***Edward Gillman,*** Naval Nuclear Laboratory

The solid to vapor phase transition boundary of any material is separated by a surface that exists at any finite temperature. To account for the internal energy due to the surface separating the solid and the vapor phases, the energy of the system is modified by a factor proportional to the surface area. A constant of proportionality, γ, which modifies the internal energy due to a surface is referred to as the surface tension or the surface free energy. Surface stress, which is directly related to surface tension, modifies the distribution of hydrogen and zirconium hydrides near the surface in Zircaloy (Zr-2, Zr-4, Zr 2.5 wt. % Nb). Depth profiling performed with Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) was able to directly identify the surface localization of hydrogen and zirconium hydride.

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