Applied Surface Science
Room 319 - Session AS-WeA

ToF SIMS in Applied Surface Science

Moderators: Dr. Jean-Paul Barnes, CEA-LETI, France, **Dr. Tanguy Terlier**, Rice University

2:15pm **AS-WeA-1 Enhancing Industrial Problem Solving with ToF-SIMS**, ***David Carr***, *Stacy Hanson,* 3M **INVITED**

Working in a central research laboratory within a large corporation presents both exceptional opportunities and unique challenges. The surface analysis facility supports every stage of product development, from fundamental research and early-stage innovation to scale-up and manufacturing troubleshooting, across an extraordinarily diverse portfolio of materials and products that extend far beyond the familiar Post-it® notes and Scotch® tape that many people associate with 3M. Because there are rarely "standard" analyses, success depends on combining technical depth with creative problem solving.

Among the available analytical techniques, time-of-flight secondary ion mass spectrometry (ToF-SIMS) is particularly valuable because of its ability to generate highly sensitive surface chemical maps and provide insight into composition both at and beneath the outermost surface of a material. These capabilities make ToF-SIMS a powerful tool for addressing a wide range of industrial materials questions, including failure analysis, process optimization, contamination identification, and structure–property investigations.

This presentation will highlight a range of topics with practical advice on methods to apply ToF-SIMS for industrial problem solving.

2:45pm **AS-WeA-3 Capabilities and Challenges of Dual-Beam Depth Profiling at Ultra-Low Sputter Energies**, *Derk Rading, Julia Zakel,* ***Thomas Grehl***, *Philipp Brüner, Wolfgang Paul, Ewald Niehuis,* IONTOF GmbH, Germany

For the majority of TOF-SIMS users, inorganic dual beam depth profiling [1] is one of the key modes of operation, particularly in the semiconductor industry where its versatility and flexibility are essential for its success. With current instrumentation, routine analyses are typically performed at 500-1000 eV sputtering energy, while the lowest energies used are in the range of 250-350 eV. The dual beam principle, with separate sputtering and analysis ion beams, enables independent optimization of the lateral resolution, mass resolution, and detection limit (high energy beam), as well as the sputtering conditions. The latter determine depth resolution, transient regime, and chemical signal enhancement. However, the dual beam mode also comes with a trade-off: to prevent the high-energy beam from degrading the depth resolution while maximizing detection sensitivity, the fluence ratio of the two beams must be carefully controlled [2].

To the best of our knowledge noextrapolation has yet been performed below 250 eV, so experiments are needed to verify the usefulness of dual beam depth profiling at these ultra-low sputtering energies. Our results show that dual beam depth profiling even at sputtering energies < 250 eV follows the trends from previous studies very nicely and no unexpected deviation is found. This study expands the knowledge beyond the currently practical energy range by identifying the fluence ratio limit required for silicon-based materials to maintain optimum depth resolution. It also examines how this limit varies with the choice of primary species and energy. Additionally, we assess the impact of different primary species on the sensitivity at the critical fluence ratio for a given sputtering energy.

The experiments were conducted on well-defined model samples, extending previous work to lower energies. Finally, we demonstrate the practical applicability of the extended energy range and optimized analytical conditions in TOF-SIMS depth profiling on a relevant real-world sample.

[1] H.-G. Cramer et al. SIMS IX, Eds. A. Benninghoven et al., Wiley, Chichester, New York (1994) 449

[2] T. Grehl et al., *Applied Surface Science* 203-204 (2003) 277–280

3:00pm **AS-WeA-4 Ultraviolet Picosecond Laser Ablation of Agar Films Evaluated by SEM and ToF-SIMS**, ***Anna Karagiannakis,*** University of Illinois at Chicago*; Anton V. Ievlev, Gabriel D. Parker,* Oak Ridge Natinal Laboratory*; Mehak Verma, Reyhane Shavandi, Luke Hanley,* University of Illinois at Chicago

Laser ablation with mid-infrared femtosecond laser pulses is used for rapid depth profiling in soft materials, but the use of ultraviolet picosecond lasers for ablation requires investigation of potential sample damage. The surface sensitivity and gaseous cluster ion beam depth profiling capability of time-of-flight secondary ion mass spectrometry (ToF-SIMS) make it ideal for tracking potential surface modification. Picosecond UV laser ablation (213 nm, 30 ps) was used to etch craters in dried agar films loaded with known metabolites on either optical grade glass slides or polished silicon wafers. Ablation crater morphology was assessed by scanning electron microscopy (SEM) across multiple power levels to identify the optimal fluence to be ~80 mJ/cm^2 for uniform and reproducible material removal on both substrates, a prerequisite for meaningful depth-resolved chemical interpretation. Higher fluences produced non-uniform crater morphologies with mechanical fracturing of the agar film, including cracking and delamination at crater edges, rendering them unsuitable for depth profiling. Negative-ion ToF-SIMS spectra were then used to compared ablated and non-ablated regions: non-ablated surfaces, representing the outermost film layer prior to ablation, were dominated by inorganic salt ions accumulated during drying: F^- (*m/z* 19), Cl^- (*m/z* 35), CN^- (*m/z* 26), CNO^- (*m/z* 42), PO_2^- (*m/z* 63), and PO_3^- (*m/z* 79), co-existing with detectable agar polysaccharide fragment ions, establishing the chemical baseline before ablation. Following ablation at the optimized power, inorganic salt signals were markedly reduced while agar-associated fragments — OH^-, C_2HO^-, $HCOO^-$, $C_2H_3O_2^-$, $C_3HO_2^-$, and $C_3H_3O_2^-$ — were retained at comparable intensities, demonstrating that ablation exposed a chemically distinct subsurface layer in which the organic matrix was preserved but the salt-enriched surface was removed. These results demonstrated the chemical changes that ablation induced through the surface of a dried agar film. Additional characterization is ongoing to further validate these findings across substrates and loading conditions. Ongoing experiments seek to determine the distribution of a metabolite doped within the agar matrix via ToF-SIMS depth profiling.

3:15pm **AS-WeA-5 3D Characterization of High-Aspect-Ratio Trench Using SIMS**, ***Dimitry Kouzminov***, *Vikram Bhosle, James Cournoyer, David Barrett, Cuiyang Wang,* Applied Materials Inc.

Achieving precise conformal doping in **high-aspect-ratio trench (HART)** structures like CMOS image sensors, 3D NAND and 3D DRAM is becoming increasingly important for next generation device performance. 1.5D SIMS has been used to characterize sidewall *dopant dose conformality* for 2 decades. This technique was developed mostly in application to FinFet transistor where trench depth typically doesn't exceed 200-300 nm and trench width is of the order of 100-150 nm[1]. 1.5D SIMS measurement, however, does not provide information on sidewall dopant concentration which is crucial for contact manufacturing in 3D DRAM process.

1.5D SIMS analysis requires a-Si trench backfill, and there are adverse effects associated with it. One of them is the loss of sidewall dopant [2].Another effect is specific to the HART itself: unfilled void in the middle of the trench due to the "bottleneck" forming at trench top during a-Si CVD deposition process. The presence of this void results in SIMS measurement artifact which appears as modulation in dopant distribution. The nature of this artifact will be discussed in the paper. To eliminate this problem, we developed primary beam trench auto-filling technique resulting in artifact-free 1.5D SIMS analysis. This technique will also be discussed in detail in the current paper.

Besides adverse effects associated with backfill void formation, HART dimension measuring from 5 to 30-40 um in depth presents a possibility for the *through-sidewall SIMS dopant distribution measurement* [3]. We call this technique ***Lateral SIMS***. This technique is introduced and in-detail discussed in the current paper. Combined analyses using combination of *Lateral SIMS* and 1.5D SIMS comprise ***3D HART dopant characterization***. Sidewall dopant distribution obtained by *Lateral SIMS* is corroborated by the correlative APT analysis which is also presented in the current paper

References:

1. J. Mody et al, J. Vac. Sci. Technol. B **28**, C1H5 (2010); https://doi.org/10.1116/1.3269755
2. D. Kouzminov et al, *Microscopy and Microanalysis*, Volume 25, Issue 2, 1 April 2019, Pages 511–516
3. D. Kouzminov, V. Bhosle et al, Patent Number: US12575379

3:30pm **AS-WeA-6 In-situ Gas Cluster Ion Beam Cryo-Sectioning to Enable Subcellular Cryo-ToF-SIMS Imaging**, *Claire Seydoux,* Univ. Grenoble Alpes, CEA, IRIG-MEM, Current address: ESRF – The European synchrotron, France*; Bérangère Moreau,* Univ. Grenoble Alpes, CEA, IRIG, MEM, France*; Michel Boujard,* Univ. Grenoble Alpes, CEA, Grenoble INP, IRIG-Pheliqs, France*; Eric Gauthier,* Univ. Grenoble Alpes, CEA, Grenoble INP,IRIG-Spintec, France*; Pierre-Henri Jouneau,* Univ. Grenoble Alpes, CEA, IRIG-MEM, France*;* ***Jean-Paul Barnes****,* Univ. Grenoble Alpes, CEA, Leti, France

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is capable of label-free molecular imaging at lateral resolutions below a micron, but the analysis of biological samples is contingent on adequate sample preparation. Conventional fixation or dehydration alters morphology and induces analyte relocation, while cryo-transfer systems are costly and not always available. We present an in situ cryo-etching approach using a gas cluster ion beam (GCIB) and a custom sample holder with a flat titanium ridge mask, enabling the sectioning of frozen specimens directly inside the ToF-SIMS instrument [1]. To illustrate the potential of this method produced flat, artifact-free surfaces suitable for subcellular imaging without chemical treatment or cryo-transfer we used Arabidopsis thaliana seeds as a model system. ToF-SIMS secondary ion images indicated that the tissue architecture was not modified by the sample preparation and distinct subcellular compartments were visible at a lateral resolution of ~1 µm. Secondary ion mass spectra contained intact molecular ion peaks up to 1000 Da This is in stark contrast to air-dried cryosections of the same model seed sample, that suffered from structural collapse and analyte delocalization. This in-situ cyo etching approach provides a practical and accessible route for cryo-ToF-SIMS analysis of hydrated biological materials, combining structural fidelity with molecular integrity. It offers an interesting alternative to conventional cryo-transfer methods for high-resolution chemical imaging and opens up the possibility for 3-D imaging by modifying the height of the mask and performing several etching and imaging cycles.

This work was carried out on the Platform for Nanocharacterisation (PFNC) of CEA-Grenoble, supported by the “Recherche Technologique de Base”, “3D-Lipid” InterCarnot Project between CEA-Leti et 3BCAR institutes and "France 2030 - ANR-22-PEEL-0014" programs of the French National Research Agency (ANR).

[1] C. Seydoux et al. J. Am. Soc. Mass Spectrom. 2026, 37, 1132−1139

4:15pm **AS-WeA-9 Advancing TOF-SIMS Workflows for Automated Mineral Grain Identification in Complex Samples**, ***Jacob Schmidt****, Siddhartha Ghosh,* Physical Electronics USA*; Susana Brito e Abreu,* University of Queensland, Australia

In mineral exploration and processing, the surface chemistry of individual mineral particles plays a critical role in separation efficiency and process performance, particularly for complex ores. Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) provides a unique capability to probe this chemistry at the scale of individual grains. However, the practical application of TOF-SIMS to large, heterogeneous mineral samples is limited by the time and effort required to locate, analyze, and identify particles of interest, which restricts throughput and statistical representativity. This work is part of a collaborative effort with the University of Queensland to advance TOF-SIMS toward a more scalable analytical approach for mineral processing applications.

To address these limitations, we have leveraged AI-assisted software development to rapidly prototype automated TOF-SIMS workflows for the identification of regions of interest. Large area Mosaic imaging is used to systematically survey samples and identify grain scale regions containing minerals of interest. Spectra from these regions are then extracted and compared to curated reference data to support mineral identification, reducing reliance on manual interpretation while improving consistency across large datasets. This approach enables particle-specific surface chemistry measurements across statistically meaningful populations, including fine and sparsely distributed target phases. These developments support the practical use of TOF-SIMS for mineral processing and contribute toward its adoption as a routine tool for studying surface chemistry drivers in complex mineral systems.

4:30pm **AS-WeA-10 Rapid Large-Area Mapping of Rare Earth Elements and Mineral Phases in Geological Samples Using ToF-SIMS**, ***Zihua Zhu****, Xin Zhang, Xiaoxu Li, Yifu Feng, Vaithiyalingam Shutthanandan, Odeta Qafoku,* Pacific Northwest National Laboratory

Rare earth elements (REEs) in geological drill core samples typically occur at trace concentrations within heterogeneous mineral hosts, creating significant challenges for rapid, phase-resolved characterization during exploration workflows. This study demonstrates that time-of-flight secondary ion mass spectrometry (ToF-SIMS), owing to its exceptional sensitivity, enables rapid, large-area mapping of REE distributions and associated anion clusters directly on polished core sections. Importantly, its high mass resolution effectively resolves spectral interferences that commonly hinder energy-dispersive X-ray spectroscopy (EDX) and synchrotron-based mapping approaches. Large-area surveys quickly identify localized REE-enriched regions, while high-resolution imaging reveals co-localization with diagnostic phosphate fragments (e.g., PO_x^-), allowing discrimination of REE host phases such as apatite and xenotime. Applied to altered Yellowstone rhyolite, ToF-SIMS reveals microscale REE enrichments that remain undetected by conventional bulk analytical and electron/X-ray-based techniques. By combining high sensitivity, minimal sample preparation, and rapid analytical throughput (<2 hours per sample), ToF-SIMS offers a powerful complementary method for rapid screening and phase-resolved REE characterization, supporting more informed early-stage exploration decisions and enabling more targeted downstream analyses.

4:45pm **AS-WeA-11 Determination of Relative Sensitivity Factors for Mg, Co, B, Be, K, and Si in Various Oxide Matrices Using Quadrupole SIMS.**, ***M. K. Indika Senevirathna****,* Clark Atlanta University*; Jacob Steele, Seungmin Lee, Anna Park, Kathy Azizie,* Cornell University*; Michael D Williams,* Clark Atlanta University*; Darrell Schlom,* Cornell University, Kavli Institute at Cornell for Nanoscale Science, Leibniz-Institut für Kristallzüchtung

Complex oxide semiconductors are of considerable interest for emerging electronic and functional device applications due to their wide range of tunable structural, electronic, and defect-related properties, which can be engineered through composition, doping, and processing conditions. In this work, matrix-dependent Relative Sensitivity Factor (RSF) behavior will be investigated using quadrupole Secondary Ion Mass Spectrometry (SIMS) in different oxide matrices, including $(Al_xGa_{1-x})_2O_3$, SnO, Al_2O_3 and Ga_2O_3, implanted with Si, Mg, Co, B, Be, and K ions. Depth-resolved SIMS profiling will be performed to examine impurity incorporation, elemental distribution, and matrix effects on secondary ion yield for quantitative analysis.

The results will show pronounced variations in RSF values as a function of both implanted species and host oxide matrix. Significant differences in secondary ion intensities, depth profile shapes, and sensitivity behavior will be observed across the investigated materials, indicating strong matrix-dependent ionization and sputtering effects. Further analysis will reveal that cobalt implantation exhibits distinct behavior compared to light and alkaline-earth species, reflecting the influence of local bonding environment and matrix composition on SIMS quantification. These findings provide important information on RSF variability across $(Al_xGa_{1-x})_2O_3$, SnO, Al_2O_3, and Ga_2O_3 systems and improve the accuracy and reliability of quantitative quadrupole SIMS analysis for the doped oxide matrices studied.

5:00pm **AS-WeA-12 In-situ thermal analysis of Pyrolyzed Polyacrylonitrile Film using operando ToF-SIMS**, ***Tanguy Terlier****,* Rice University, Department of Chemical & Biomolecular Engineering, Shared Equipment Authority*; Khalid Alkandery, Sibani Lisa Biswal,* Rice University, Department of Chemical & Biomolecular Engineering

Emerging technologies increasingly depend on complex multifunctional materials whose performance and reliability are strongly governed by their chemical composition, interfacial chemistry, diffusion behavior, degradation pathways, and thermally induced transformations. Understanding these mechanisms is essential for both fundamental research and industrial implementation; however, the structural and chemical complexity of advanced materials remains difficult to probe using conventional characterization techniques.

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) has become a powerful surface analytical technique capable of providing highly sensitive elemental and molecular information from surfaces, interfaces, thin films, and three-dimensional architectures. Recent advances in ToF-SIMS instrumentation now enable operando investigations under realistic reaction environments, offering new opportunities to directly monitor dynamic thermal and chemical processes in functional materials.

In this work, we present an operando thermal analysis methodology based on ToF-SIMS for investigating thermally driven reactions through controlled in-situ heating during analysis. As an initial demonstration, a reference polystyrene film is annealed to illustrate how operando thermal SIMS can probe both physical and chemical transformations. We then investigate pyrolyzed polyacrylonitrile (pPAN) films, a conductive binder widely used in lithium-ion batteries. Owing to its high elasticity, pPAN has shown significant potential for silicon-based anodes. Here, we examine the

evolution of aromatic and aliphatic secondary ion fragments as a function of temperature and demonstrate how their relative intensity ratio can be used to monitor the pyrolysis behavior of the material under various annealing conditions. The ToF-SIMS results are correlated with thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) and Fourier-transform infrared spectroscopy (FTIR) to validate the operando thermal analysis approach.

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