Applied Surface Science
Room 319 - Session AS-TuM

Applied Surface Science in Action I

Moderators: Dr. Michael Eller, University of Mississippi, **Dr. Samantha Rosenberg**, Kairos Power

11:00am **AS-TuM-13 Considerations when Developing Standards and Tools for Surface Chemical Analysis***, **Justin Gorham**, Donald Windover,* National Institute of Standards and Technology (NIST) **INVITED**

Surface chemical analysis, like other disciplines, rely on harmonized methods and benchmarking materials in order for results from the same technique to be reproducible from institute to institute. These harmonized methods are often incorporated into documentary standards which contain the details analysts require to conduct a process (e.g. prepare sample(s); calibrate the tool(s); conduct the measurement(s); analyze data; reporting requirements; etc.). Benchmarking materials are often co-developed during standards work as either a classification of reference materials or simply materials of known purity. As the name implies, these benchmarking materials are often employed as a tool for checking/calibrating a given property of a tool (e.g. linearity of energy scale). This presentation will focus on considerations and tools employed in the development of standards from a surface analysis perspective. Discussion will be held on both the development and maintenance of standards. Additionally, discussion will focus on the use case of NIST benchmarking materials known as research grade test materials (e.g. Hafnium oxide, Titanium Nitride, etc), currently under development, to advance measurements in the semiconductor community specifically as it pertains X-ray based measurements (e.g. XRR, XPS, XRF).

11:30am **AS-TuM-15 Might a Tiered Approach to Reviewing and Reporting Help Improve the Quality of XPS Results Appearing in Publications?***, **Don Baer,*** Pacific Northwest National Laboratory

Anecdotal evidence, confirmed by detailed analysis, highlights widespread inadequacies in XPS data and analysis reported in scientific literature. As XPS is increasingly utilized across various fields, researchers without specialized XPS knowledge often collect, analyze, and report data. These papers are often reviewed by experts in the subject matter, not in XPS, leading to missing or incomplete instrumental, data, and analysis information appearing in journals. Consequently, the quality and reliability of XPS results are difficult to assess, and flawed data is frequently published. Although this issue is not unique to XPS, this talk focuses on the reviewing and reporting of XPS information.

Surface analysis experts have worked to provide guidelines for less experienced XPS users. However, there remains a gap between the information reported in journals, what would comply with ISO and ASTM standards, the expectations of reviewers, and what is really needed. Research by Karel Gaskel revealed that most standard-required information is not reported, reflecting a disconnect between ideal reporting practices and practical journal requirements. Standards often focus on full repeatability, which can be burdensome and not always relevant, yet more information is needed than is typically provided to ensure data quality and relevance.

To address these challenges, a tiered approach to reviewing and reporting XPS data is suggested for discussion. A model might include three levels: i) **Credibility Level:** Data follows generally accepted practices and is adequate for its stated purpose in journals or reports, especially when XPS is not a primary analysis method used in the paper; ii) **Archive Level:** Data and analysis are of high quality, with sufficient detail about the instrument, sample, and analysis to allow for inclusion in databases and to provide context and purpose; **Reference/Fully Repeatable Level:** Full information is provided, enabling experts to replicate experiments and qualify the data as "reference data" of standard quality.

The need for thorough and appropriate reporting grows as artificial intelligence and data archiving become more prevalent. Adequate information is necessary for AI systems to identify high-quality data, and for archives to maintain meaningful records. A tiered approach might offer a practical guide for improving both the reporting and review of XPS data, aligning reporting requirements with the intended use and ensuring data quality across various applications. The challenge is identifying what each of these, or other, levels would mean in practice and how they might be described with clarity.

11:45am **AS-TuM-16 Strategies for Reducing Charging of Insulating Samples in Auger Electron Spectroscopy***, **Juergen Scherer,*** Physical Electronics

Auger Electron Spectroscopy (AES) is a powerful surface-sensitive analytical technique widely used to probe the elemental and chemical composition of materials at the nanoscale. Its high spatial resolution makes AES uniquely valuable for applications ranging from microelectronics and thin films to failure analysis and advanced materials. However, a persistent challenge in AES is the analysis of materials that are insulating or contain insulating regions, which represent a large and growing fraction of technologically relevant materials. Charge accumulation under electron beam irradiation can lead to spectral distortion, peak shifting, signal loss, and, in severe cases, the inability to obtain meaningful data.

This presentation discusses practical strategies for reducing and managing charging effects during AES analysis of insulating and heterogeneous samples. Emphasis is placed on understanding the physical origins of charging phenomena and how instrument configuration, experimental conditions, and sample preparation choices can be leveraged to mitigate their impact. Through illustrative examples, the talk highlights how thoughtful control of measurement parameters can substantially improve data quality, reproducibility, and reliability when working with challenging samples. By focusing on realistic scenarios encountered in routine AES measurements, this work aims to provide users with actionable insights for extending the applicability of AES to a broader class of insulating and heterogeneous materials.

12:00pm **AS-TuM-17 The Binary Residual Map and the Automated Determination of the Transfer Function Cutoff for the Fourier Filtering of X-ray Photoelectron Spectroscopy Data***, **Matthew Linford**, Alvaro Lizarbe, Maksym Gerashchenko, Tyler Andersen, Jonathan Nelson,* Brigham Young University*; David Aspnes,* NC State

We recently proposed that the Fourier denoising of X-ray photoelectron spectroscopy (XPS) data may have a legitimate place in XPS data processing (*J. Vac. Sci. Technol. A,* **2025**, *43*, 033401). For example, the denoising of spectra becomes critical when they are to be used for training artificial intelligence (AI) systems. In this talk, we discuss two new data analytical tools we have developed that greatly facilitate the Fourier denoising of XPS and other types of data. The first is the Binary Residual Map™. The binary residual map color codes the residuals from large numbers of fits or smooths and combines them into a single figure. The transition in a binary residual map where longer runs of a single color disappear is generally where good fitting or denoising is taking place. In addition, we have developed an algorithm, which we will discuss, that finds a reasonable position for the transfer/filter function in reciprocal space for denoising. This feature will be important both for newer users that may be unsure about Fourier analysis and also for fully automating the denoising of XPS data.

Applied Surface Science
Room 319 - Session AS-TuA

Applied Surface Science in Action II

Moderators: Dr. Hong Piao, FUJIFILM Electronic Materials USA., Inc., **Dr. Jeffrey Terry**, Illinois Institute of Technology

2:15pm **AS-TuA-1 Quantification of Surface Functional Groups on Nano- and 2D Materials***, Jörg Radnik,* Federal Institute for Material Research and Testing (BAM), Germany **INVITED**

Surface chemistry plays a crucial role in determining the properties of nanoforms. Incorporation into a matrix, solubility, and dispersibility are all strongly influenced by their surface. Therefore, measurements of surface functionalization are essential for nanoforms, both in terms of applicability and regarding safety and sustainability. Despite this importance, the reliable quantification of functional groups on nanoforms remains a challenge. Documentary standards have recently been published or are currently under development, proposing X-ray photoelectron spectroscopy (XPS) as one of the key methods.[1]

In developing protocols for the quantification of surface functionalities, we chose two approaches: (i) correlative measurements, in which the same samples were analyzed using at least two different methods, and (ii) interlaboratory comparisons (ILCs) carried out across multiple laboratories. Both approaches were successfully applied to functionalized graphene nanoplatelets. The comparison of XPS and energy-dispersive X-ray spectroscopy (EDS@SEM) results shows good agreement between the two methods when the different analysis volumes are considered.[2] The international ILC with XPS as method revealed a pronounced influence of excessively high humidity and sample preparation on the results.

XPS and quantitative nuclear magnetic resonance (qNMR) measurements were carried out on aminated silica nanoparticles, enabling a correlation between the N/Si ratio determined by XPS and the amine coverage on the nanoparticle surface derived from NMR.[3] Comparative measurements performed in two laboratories yielded comparable results. Based on the results obtained, uncertainty budgets could also be established.

We thank for the financial support of the projects ISO-G-Scope (19NMR04) and SMURFnano (23NMR02) the European Partnership on Metrology and of the projects ACCORDs (grant agreement 101092796) and GrapheneEU (grant agreement 101119461) the European Union's Horizon Programme.Views and opinions expressed are however those of the author only and do not necessarily reflect those of the European Union or EURAMET. Neither the European Union nor the granting authority can be held responsible for them.

References:

[1] ISO/TS 23359:2025 Nanotechnologies – Chemical characterization of graphene-related 2D Materials from powders and liquid suspensions

[2] Mrkwitschka, P. et al. Small 22 (2026) e11283 DOI: 10.1002/smll.202511283

[3] Tavernaro, I. et al. Nanoscale Adv. 7 (2025) 6888 DOI: 10.1039/D5NA00794A

2:45pm **AS-TuA-3 Compositional Analysis of Al1-XScXN Thin Films***, Jeffrey Shallenberger, Saeed Almishal, Jon-Paul Maria,* Penn State University*; G. Bruce Rayner,* Kurt J. Lesker Company

Aluminum scandium nitride ($Al_{1-x}Sc_xN$) has received a lot of attention because of its ferroelectric properties and ability to be integrated on silicon. It has been synthesized over a wide compositional range by a variety of growth and deposition techniques including sputtering, molecular beam epitaxy (MBE) and atomic layer deposition (ALD). Determination of the composition of $Al_{1-x}Sc_xN$ thin films has been done by a variety of techniques including: SEM-EDS, XRF, RBS, SIMS and XPS. This talk will focus on the use of XPS to characterize both thin (~30 nm) and thick (300 nm) films produced by ALD and sputtering, respectively. XPS offers depth-resolved compositional information which is important as these films frequently have AlN layers to improve epitaxial growth or are grown on sapphire substrates. EDS, XRF and RBS have relatively poor depth resolution making it difficult or impossible to determine the stoichiometry in these cases, particularly on very thin films. Accurate measurement of oxygen content is also important as high levels of oxygen can degrade the ferroelectric properties. We utilize Rutherford backscattering (RBS) to help calibrate the XPS-derived stoichiometry of a series of $Al_{1-x}Sc_xN$ films ($0.58<x<0.15$). This talk will also discuss the relative advantages and disadvantages of the commonly utilized thin film compositional techniques with a goal of providing guidance to users when selecting an analytical tool.

3:00pm **AS-TuA-4 Surface-Engineered Nanostructures for Wastewater Contaminants Sensing and Its Treatment by Thermocatalysts***, Zong-Hong Lin,* National Taiwan University, Taiwan*; **Jinn P. Chu,*** National Taiwan University of Science and Technology, Taiwan

Ensuring access to clean water is a critical global health challenge, yet the energy required for contaminant monitoring and treatment intensifies resource pressures. Self-powered sensing and remediation systems offer a sustainable path forward. This study introduces multifunctional surface-engineered metallic nanotube arrays (MeNTAs) as a tunable platform for both pollutant detection and degradation. By tailoring composition and structure, we controlled surface wettability across a wide range (5°–144°) to suit specific functions.For detection, a Ni-W-Ni MeNTA with optimal triboelectric output was integrated into a droplet-mode liquid-solid triboelectric nanosensor (DLS-TENS). Modified with ion-selective membranes, it rapidly (20 ms) and sensitively detected heavy-metal ions (Cr^{6+}, Pb^{2+}, Hg^{2+}). For bacterial sensing and thermocatalytic treatment, W-SS MeNTAs were employed. Their hydrophilic stainless-steel nanoparticles enabled in-situ synthesis of aptamer-functionalized gold nanoparticles for highly sensitive E. coli detection (163 mV/decade). Simultaneously, surface Fe^{2+} ions catalyzed •OH radical generation via the Fenton reaction, while adhered Bi_2Te_3 nanoflakes generated H_2O_2 under a small thermal gradient (10 °C). This system achieved significant bacterial inactivation (E. coli: 97%; S. aureus: 95%) and 95% Cr^{6+} reduction.To demonstrate practical utility, we constructed a wireless sensing bottle for real-time wastewater analysis and integrated it with a treatment module for on-site, simultaneous monitoring and purification. This work presents a cost-effective, portable, and self-powered platform, highlighting the strong real-world potential of multifunctional MeNTAs for advanced water purification.

3:15pm **AS-TuA-5 Multi-Technique Structural and Chemical Characterization of Native Oxide Evolution on Niobium Thin Films for Nasa Astrophysics Detectors***, **FEMI AKINRINOLA**, Robbyn Trappen, Nethmi Loku Kankanamge, Tap Raj Bhandari,* West Virginia University, USA*; Thomas Stevenson, Emily Barrentine,* NASA Goddard Space Flight Center*; Mikel Holcomb,* West Virginia University, USA

Niobium-based superconducting detectors, including microwave kinetic inductance detectors (MKIDs) and transition-edge sensors (TESs), are critical for future NASA astrophysics missions operating in the far-infrared to microwave spectral range. Their performance can be strongly influenced by native oxide formation and surface chemical modifications introduced during fabrication and post-processing. Building on our previous X-ray absorption spectroscopy (XAS) investigation of niobium oxide formation in superconducting device structures, we present an expanded study combining XAS with grazing-incidence X-ray diffraction (GIXRD) and X-ray reflectivity (XRR) to obtain complementary chemical and structural information from the near-surface region of Nb thin films.

This work examines Nb films subjected to multiple surface-processing conditions relevant to superconducting device fabrication, including pristine films, buffered oxide etch (BOE) treatments, unbuffered HF treatments, and hydrogen-exposure conditions. Oxygen K-edge XAS is used to probe changes in the local electronic structure and bonding environment associated with oxide evolution, while GIXRD measurements at multiple incidence angles are used to evaluate crystalline phase formation and structural changes near the film surface. XRR measurements provide additional information on film thickness, interface quality, density, and surface roughness. Preliminary XRR analysis indicates that the films remain structurally dense after processing while supporting thin oxide-like surface layers, whereas GIXRD measurements show that crystalline metallic Nb remains the dominant phase in the films studied thus far.

Rather than relying on a single characterization technique, this combined approach is intended to provide a more complete understanding of how different fabrication and surface-treatment conditions influence oxide evolution, crystallinity, and near-surface structure in Nb-based superconducting materials. Ongoing analysis is focused on correlating spectroscopic trends observed in XAS with structural information obtained from GIXRD and XRR across the different processing conditions. These results contribute to NASA's broader effort to better understand and optimize superconducting detector fabrication processes for future space-based astrophysics missions.

We acknowledge support from NASA 80NSSC22M0173 and NSF 2417349.

4:00pm **AS-TuA-8 Interfacial Solution Structure Impacts Crystal Growth, Ice Nucleation, and Particle Aggregation***, **Elias Nakouzi,*** Pacific Northwest National Laboratory*; Mingyi Zhang,* University of Oklahoma*; Kuan-Ting Liu, Dong June Jang,* Cornell University*; Philip Brahana, Bhuvnesh Bharti,* Louisiana State University*; Jaehun Chun,* Pacific Northwest National Laboratory*; Ulrich Wiesner, Lara Estroff,* Cornell University **INVITED**

Solution structure at solid-liquid interfaces creates inter-particle forces and chemical potential gradients that influence particle stability, reactivity, and aggregation. However, despite this relevance to a variety of research fields, significant knowledge gaps remain in our understanding of solid-liquid interfaces at the molecular scale. Using a combination of atomic force microscopy, confocal fluorescence microscopy, colloidal theory, and atomistic simulations, we present three case studies examining the effect of interfacial solution structure on particle aggregation, crystal growth, and heterogeneous nucleation. Firstly, we determined that extreme salt concentrations enhance ion correlations at the surface of boehmite nanoparticles, resulting in strong repulsive forces at short particle separations that decrease the rate of particle aggregation. In the second study, we investigated the incorporation of ligand-coated nanoparticles in growing calcite crystals. This process is governed by the interactions experienced by an incoming particle as it penetrates the interfacial hydration layers, as well as the binding energy upon adsorption to the growing crystal surface. Thirdly, we determined that oxidizing a polymer surface results in the assembly of hydration layers at the polymer-water interface, which increase the surface hydrophilicity and the propensity for nucleating ice. We anticipate that these studies will provide insights into the molecular nature of solid-liquid interfaces with important implications on relevant problems in geochemistry, electrochemistry, and materials synthesis.

4:30pm **AS-TuA-10 Surface Distribution, and Thermal Evolution in Nuclear Graphite: What We Can Learn Using XPS***, **Jonathan Counsell,*** Kratos Analytical Limited, UK*; Chris Moffitt,* Kratos Analytical Inc.

Analysis of material samples related to nuclear industry remains an important research area considering the rapid evolution of new nuclear power plants planned for the coming century. Critical in these systems is the neutron moderator material graphite. Understanding the interaction of high-energy particles radiation and these effects on structure and chemistry of the graphitic lattice.

XPS is used to analyse the changes in sp2/sp3 character under high-energy Cs ion bombardment and the relationship between dose and depth of change for impinging ions. We will discuss not just structural changes but also chemical relationships between the ions present in the near-surface region and the constituent graphite. We will show how HAXPES can be used to gain insight also.

The life cycle of a graphitic rods in a reactor involves withstanding harsh environments, therefore, considering the operating environment, we explore the effects of heating to determine possible thermal effects from thermal cycling. Here we will exploit different options for analysis including in-situ thermal treatments of the surface to understand the processes occurring in the surface and the stabilisation of incorporated ions. We will introduce best practices and experimental design considerations to optimise and probe the process taking place.

4:45pm **AS-TuA-11 Energy Materials and the Importance of Cryo-XPS***, **Liam Soomary,*** Kratos Analytical Limited, UK*; Chris Moffitt,* Kratos Analytical Inc.

The development of advanced energy storage materials is crucial for the transition to sustainable energy solutions. Cryogenic X-ray Photoelectron Spectroscopy (cryo-XPS) plays a pivotal role in understanding the surface chemistry and electronic properties of these materials under extreme conditions. This study focuses on vitrification techniques to preserve the transient states of energy storage materials, allowing for accurate characterization before degradation occurs.

Using cryo-XPS, we investigate the surface distribution and chemical composition of various energy storage materials, capturing transient states and reducing beam damage through optimized sample preparation and analysis protocols. Software workflows, developed for specific sample types are utilized to streamline the data acquisition and post-processing steps, ensuring reproducibility and reliability of the results. Additionally, vacuum damage is minimized by employing cryo conditions, which are critical for maintaining the integrity of the sample during analysis.

This work highlights the importance of cryo-XPS in providing detailed insights into the surface properties of energy storage materials, enabling the identification of key mechanisms governing their performance. By integrating vitrification, software workflows, and vacuum optimization, we aim to advance the understanding and development of next-generation energy storage technologies.

5:00pm **AS-TuA-12 In-Vacuo Detection of Ti Hydride Using Advanced XPS Technique***, **Ravi Prakash,*** *Jacqueline van Veldhoven,* Semicon Equipment Lifetime, TNO, the Netherlands Organisation for Applied Scientific Research, Netherlands*; Herman Bekman, Leon Arkesteijn,* Semicon Equipment Metrology, TNO, the Netherlands Organisation for Applied Scientific Research, Netherlands*; Ronald Hultermans, Violeta Navarro Paredes, Mark van de Kerkhof,* ASML, Veldhoven, Netherlands

Titanium has an outstanding strength-to-density ratio, high tensile strength, and is naturally resistant to chemical corrosion. Due to the favourable mechanical properties in harsh environments, titanium is widely used in chemical processing equipment, aerospace structures and marine systems. However, when it is exposed to environments with H_2-gas/H-radicals/H-ions, hydrogen may diffuse into the bulk titanium and start forming hydrides which leads to embrittlement, posing a significant risk under extreme conditions.

To measure hydride formation in titanium in-vacuo is crucial. ToF-SIMS and EBSD are ideal techniques to detect the hydrides, but using these techniques requires a very specific combination of exposure and analysis techniques which is not very common. If a hydride containing Ti sample is exposed to air, the surface state may alter, which limits the ability to detect early stage hydride formation on the surface. Also, our investigation shows that titanium oxidizes rapidly even under UHV conditions.

This work introduces a novel in-situ methodology for detecting titanium hydride using X-ray photoelectron spectroscopy (XPS) focused on valence band measurements. A plasma/radical exposure tool attached to an XPS setup enables in-vacuum sample transfer, which allows to study hydrogen ingress in a controlled environment during exposure to H-plasma/H-radicals/H_2-gas. The approach uses a peak fitting model to isolate the overlapping oxygen and titanium hydride signals in the valence band region. Correlating this signal with the oxygen O 1s content enables the identification of hydride formation. This method reliably differentiates between hydride-containing and hydride-free samples, allowing for the early-stage detection of embrittlement precursors after hydrogen exposure. This method not only improves detection sensitivity but also streamlines the experimental workflow by eliminating the need for additional ex-situ measurements. This allows for quicker testing of more representative samples that could contribute to enhancing lifetime.

References;

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5:15pm **AS-TuA-13 Chemical Mapping of sub-Monolayer Oxygen Functionalities on Acid Treated HOPG Surfaces Through Photo-Induced Force Microscopy***, **David Morgan,*** Cardiff University, UK

Carbon is widely used as a support for heterogeneous catalysts because of their relatively low cost, high surface area and the ease with which precious metals can be reclaimed from the support at the end of the catalyst's active life [1]. In most cases, these carbons are acid washed, before the adsorption of the active component. The wash serves two purposes; it removes unwanted inorganic contaminants present in the carbon; and it introduces oxygenated functionalities that modify the behaviour of the carbon towards the adsorption of the active component and the reaction solvent [2].

Our previous work using HOPG as a model substrate has shown HCl and HNO_3 has a significant impact on the surface topography through intrusion by the acid into the graphite, causing weakening and breakage of the interplanar bonds [3]. Chemical derivatisation studies via XPS, has shown that depending on the acid, the surface forms hydroxyl, carbonyl and nitrate containing functions, however, to date the location of these features, especially with relation to the protrusions are unknown [4].

Herein, we present the first Photo-Induced Force Microscopy (PiFM) studies of acid treated HOPG surfaces allowing the unambiguous correlation of surface topography with sub-monolayer oxygen functionalities through chemically distinct vibrational spectra.

References

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5:30pm **AS-TuA-14 The XPS of Azines: Relationship to Chemical Bonding**, ***Paul S. Bagus***, University Of North Texas, United States Minor Outlying Islands (the)*; Connie J. Nelin,* Cosultant

The properties of several azine molecules, particularly their XPS spectra, are examined. These molecules contain one, two, or three nitrogen atoms positioned in either equivalent or inequivalent sites within the benzene ring, where N replaces a C–H unit. The primary objective is to determine the extent to which C(1s) and N(1s) XPS can be used to identify specific molecular species and whether these spectra can be directly related to chemical bonding. The analysis focuses on binding energies (BEs) and relative intensities, I_{rel}. Interpretation of the spectra requires theoretical input because the observed XPS features include contributions from inequivalent atoms whose energy splittings, often on the order of ~1 eV, are near or below the resolution limit of standard measurements. To address this, Dirac Hartree-Fock calculations are used to obtain wavefunctions for both initial states and core-hole final states, providing reliable estimates of BE shifts and relative intensities. While our results are specifically for the azines whose spectra are analyzed, they have important implications for the interpretation of the XPS of other compounds. A key question is whether final-state effects are approximately constant across different atoms and molecules. If so, Koopmans' Theorem. which neglects relaxation, may be sufficient to relate XPS to chemical bonding; otherwise, explicit treatment of relaxation effects is required. Additional factors such as bond length variations and environmental effects are also considered. The focus will be on the main XPS features but excitations that would lead to satellite features are also considered. Pyrazine ($C_4N_2H_4$), which has only one inequivalent nitrogen and one inequivalent carbon atom, serves as a reference system. Its relatively simple spectrum aids in interpreting more complex molecules such as pyridine and pyrimidine, each of which contains three inequivalent carbon atoms and Triazines, with additional inequivalent atoms.

Applied Surface Science
Room 319 - Session AS-WeM

Advances in Sputtering

Moderators: Dr. Alexander Shard, National Physical Laboratory, **Dr. Lyndi Strange**, Pacific Northwest National Laboratory

8:00am **AS-WeM-1 Non-destructive XPS Depth Profiling Using a Three-Anode HAXPES Source with Simultaneous (Angle-Resolved) Data Collection over a Range of Angles**, ***Max Clark,*** Brigham Young University*; Paul Dietrich,* SPECS Surface Nano Analysis GmbH, Germany*; Joshua Pinder,* specs Surface Nano Analysis GmbH*; Andreas Thissen,* SPECS Surface Nano Analysis GmbH, Germany*; Matthew Linford,* Brigham Young University

In traditional X-ray photoelectron spectroscopy (XPS), depth profiling is achieved by alternating analysis scans with sputtering of the outermost layer, although at the cost of a damaged sample and increased analysis time. Angle-resolved XPS (ARXPS) can produce information at shallower depths nondestructively, but it is still constrained by the information depth (mean free path) of the photoelectrons. Using HAXPES sources and simultaneously collecting data from a range of angles (10 - 70 degrees with respect to the surface normal) increases information content, depth, speed and allows the user to see deeper into a sample. In particular, by collecting angle-resolved measurements with three X-ray sources (Al Kα, Ag Lα, and Cr Kα) focused at the same spot, non-destructive depth profiling from ca. 0 - 30 nm can be achieved with good resolution and reasonable speed. This technique has been demonstrated on samples with variable compositions and film-thicknesses.

8:15am **AS-WeM-2 XPS Depth Profiling of Multilayer Stacks using Femtosecond Laser Ablation (fs-LA)**, ***Charlie Chandler,*** University of Surrey, UK*; Dhilan Devadasan, Paul Mack, Robin Simpson, Tim Nunney,* Thermo Fisher Scientific, UK*; Mark Baker,* University of Surrey, UK

Multilayer stacks of different materials are commonly employed across a wide range of technical fields. XPS depth profiling of multilayers has been investigated previously using traditional ion beam sputtering techniques, with rotation of the sample during etching increasing the depth resolution. With the recent introduction of femtosecond laser ablation (fs-LA) as a novel depth profiling method, it is important to optimise the analytical approach to enhance depth resolution. A femtosecond laser with a 1030 nm peak wavelength, pulse length of 160 fs and top-hat optical beam shaper has been employed to perform the XPS depth profiles. Results will be shown for different classes of material using analytical set-ups with and without laser polarisation rotation and sample rotation. Discussion of the results will consider the origins of crater roughening in fs-LA depth profiling, influence of top-hat uniformity, material related effects and describe the best analytical approach for optimisation of depth resolution.

8:30am **AS-WeM-3 Calibration of Removal Rates for fs-Laser Ablation XPS Depth Profiling**, ***Tim Nunney,*** Thermo Fisher Scientific, UK*; Charlie Chandler,* University of Surrey, UK*; Robin Simpson, Paul Mack,* Thermo Fisher Scientific, UK

Femtosecond laser ablation offers new opportunities for XPS depth profiling. It has been shown that by using an ultra-fast laser for removing material from the surface, chemical damage and other effects that can distort the measured composition in an ion beam profile can be avoided [1]. For example, a tantalum nitride layer that has been deposited on silicon, with a stoichiometry of Ta_2N_3 measured by Rutherford backscattering spectroscopy, retains that composition through a fs-laser depth profile, but shows depletion of nitrogen during a monatomic ion beam profile [2]. With the introduction of this method, there is a necessity to understand the relationship between the laser energy and the ablation rate, to be able to control the removal process to match experimental requirements of the sample. This presentation will describe a simple method to determine the ablation threshold of a material, and how to use the threshold to determine the laser energy required to remove the desired amount of material per laser shot.

1. M.A. Baker et al, Applied Surface Science 654 (2024) 159405
2. C.W. Chandler et al, Applied Surface Science Advances, 34 (2026) 101008

8:45am **AS-WeM-4 IR Femtosecond-Laser Ablation of IR-Transparent Coatings - Consequences for XPS Depth Profiling**, ***Miroslav Michlicek,*** Thermo Fisher Scientific, Czechia*; Paul Mack,* Thermo Fisher Scientific, UK*; Veronika Hammerova,* Thermo Fisher Scientific, Czechia

Femtosecond-laser depth profiling is emerging as a practical complement to ion sputtering for XPS analysis of materials that are either difficult to profile by conventional monoatomic or cluster ion beams, or to simply speed up the depth profiling process. In our current implementation - Hypulse, ultrashort IR (1030 nm) pulses remove material rapidly while minimizing the extended collision cascades, preferential sputtering, and chemical reduction often associated with ion sputtering. The ablation rate, crater growth and material removal uniformity are largely defined by the energy distribution of the shaped laser beam relative to the material ablation threshold. For quantitative XPS depth profiling, this creates a fundamental tradeoff between removal rate and crater uniformity.Notably for IR transparent materials, the ablation threshold can be relatively large and easily above the ablation threshold of the substrate. In sample configurations where the overlaying thin film transmits the beam while the substrate is ablated, generally the interface tends to fail, leading to thin film tearing or lateral crater growth from point defects. Here, we investigate this behavior on a simple model of SiN on Si. The results show the described non-uniformity near the ablation threshold, however, due to the non-linear nature of the ablation process, we can largely mitigate it by a significant increase in the pulse energy.

9:00am **AS-WeM-5 AFM Analysis of Surface Morphology and Grain Growth in Ag Thin Films Prepared by RF Magnetron Sputtering**, ***Kenneth Lathrum,*** *Samuel Goutierrez, Jhonatan Gil Romero, Seonhee Jang,* University of Louisiana

Silver (Ag) thin films have unique electrical and optical properties that make them more desirable than other metals in applications such as solar cells, semiconductor chips, and optical coatings. The properties of these films depend significantly on surface morphology, uniformity, and thickness. Atomic Force Microscopy (AFM) is frequently used to analyze these characteristics at a sub-nanometer level. AFM measurements can be performed in either contact mode or tapping mode, distinguished by the positioning and movement of the cantilever beam. In contact mode, the cantilever tip maintains physical contact with the film's surface. In tapping mode, the tip is held a few nanometers above the film's surface and oscillates near its resonant frequency.

In this study, Ag thin films were prepared on n-type Silicon (Si) wafers (with a resistivity of 1-10 Ω cm) using radio frequency (RF) magnetron sputtering. The sputtering deposition process varied the plasma power and reactor pressure. Following deposition, the films were subjected to various thermal and laser annealing conditions. AFM measurements were conducted in tapping mode to prevent damaging the film surface. Gwyddion software was used to process the AFM measurement data, specifically utilizing equivalent disc radius analysis to characterize the grain distribution. This analysis is particularly useful for comparing grain distribution across different samples, such as those subjected to varying deposition parameters or annealing conditions. The equivalent disc radius is calculated using Gwydion's watershed method through the following steps: (1) determination of the grain area, (2) transformation of the grain area into an equivalent circle, and (3) calculation of the equivalent circle radius.

It was determined that the surface morphology, thickness, and electrical properties of the Ag thin films were significantly impacted by the deposition plasma power, reactor pressure, and annealing conditions. As deposition power increased, grain size, crystallite size, surface roughness, and film thickness increased, while sheet resistance decreased. In comparison, as deposition pressure increased, surface roughness and sheet resistance increased, while grain size, crystallite size, and film thickness decreased. Following thermal and laser annealing, grain size and crystallite size increased, while surface roughness, film thickness, and sheet resistance decreased. These results demonstrate that RF magnetron sputtering deposition parameters can be optimized and combined with post-deposition annealing to precisely tune the electrical and optical properties of Ag thin films.

9:15am **AS-WeM-6 Non-Destructive Depth Profiling with a Multi-Colored Monochromated X-Ray Source**, ***Paul Dietrich,*** *Emilie Gérouville, Andreas Thissen,* SPECS Surface Nano Analysis GmbH, Germany

X-ray photoelectron spectroscopy (XPS) is a powerful technique to gather information on elemental composition and chemical states of sample surfaces. Modern thin film architectures, multilayer devices, and buried

interfaces have become increasingly relevant for various fields such as semiconductor technology and energy materials. Therefore, the need to characterize chemical states deeper than the topmost surface layers grows significantly.

Ion sputtering depth profiling is a well-established approach to access deeper layers but is inherently destructive and alters chemical states and morphology of the surfaces under investigation. Non-destructive alternative is to extend into hard X-ray photoelectron spectroscopy (HAXPES). Higher photon energies increase the kinetic energy of emitted photoelectrons, which extends their inelastic mean free path and enables access to deeper layers without modifying the sample.

Traditionally, accessing multiple excitation energies and/or hard X-rays requires either synchrotron beamtime or the use of several separate X-ray sources. Unfortunately, these impose accessibility, cost, and experimental complexity constraints. We present an extended compact, small spot monochromated X-ray source that integrates up to four anode materials and their corresponding individually optimized crystal optics within a single Rowland circle-based housing. This all-in-one design enables fully automated, software-controlled in-situ switching between multiple excitation energies spanning from soft to the hard X-ray regime.

By combining measurements at different photon energies with parallel detection angle-resolved XPS (PARXPS), comprehensive depth-resolved chemical information can be obtained non-destructively from a single measurement session. The approach of PARXPS with variable excitation energy provides complementary information depths, allowing for reliable layer thickness determination and chemical state analysis from the surface through to deeper buried layers. We demonstrate the capabilities of this variable energy PARXPS approach with the latest results on different samples including (multi)layer stacks, highlighting how the combination of multiple excitation energies can study depth-dependent chemistry.

9:30am **AS-WeM-7 Evaluating Oxygen Gas Cluster Ion Beams for Inorganic Depth Profiling in Tof–Sims***, **Thierry Conard**,* IMEC, Belgium*; Wilfried Vandervorst, Claudia Fleischmann,* imec and KU Leuven (University of Leuven), Belgium

Large gas cluster ion beams have enabled major advances in ToF–SIMS depth profiling by strongly reducing sputter–induced damage and preserving molecular information in organic materials. However, their application to heterogeneous systems containing inorganic components remains problematic. Previous work using Ar gas cluster ion beams has shown that, despite the low energy per atom, depth profiling of inorganic layers is often limited by strong profile broadening arising from roughness development, ion–beam–induced mixing, and unexpectedly large information depths. Whether chemically reactive gas cluster ion beams can modify these limitations remains an open question.

In this work, we investigate the hypothesis that oxygen gas cluster ion beams alter the sputtering dynamics of inorganic materials sufficiently to change erosion behavior, mixing, and apparent depth resolution compared to inert Ar clusters. A model system consisting of aluminum delta layer(s) embedded in a silicon matrix is employed, providing a sensitive probe of sputter–induced mixing and interface distortion. Depth profiles acquired using oxygen cluster sputtering are systematically compared to reference data obtained with Ar clusters under comparable total cluster energies.

The study examines how the introduction of chemical reactivity through oxygen cluster bombardment influences profile shape, signal stability, and the apparent information depth of the delta layers. Particular attention is paid to separating the contributions of roughness development, ion–beam–induced mixing, and chemical modification to the observed depth profiles. The effects of key experimental parameters, including total cluster energy and sample rotation, are evaluated to assess whether trends previously observed for Ar clusters remain valid for oxygen clusters.

By benchmarking oxygen cluster sputtering against an established Ar–cluster reference system, this work aims to establish whether reactive gas cluster beams provide tangible advantages for inorganic depth profiling or introduce new sources of artefacts. The results are intended to define practical operating regimes and limitations for the application of oxygen cluster ion beams to heterogeneous and inorganic material systems in ToF–SIMS.

9:45am **AS-WeM-8 Low-k SiOC Etching: Correlating Surface Reaction Mechanisms with SiOC/poly-Si Etching Selectivity***, **Sang-Jin Chung**,* University of Maryland, College Park*; Pingshan Luan, Adam Pranda, Yusuke Yoshida,* Tokyo Electron America, Inc.*; Gottlieb S. Oehrlein,* University of Maryland, College Park

Front-end low-k dielectric materials, such as SiOC, are important in complementary field-effect transistors (CFET) for reducing RC and LC delay, minimizing power consumption, and mitigating crosstalk. During CFET fabrication, maximizing SiOC etch selectivity to the underlying poly-Si is crucial. To this end, a better understanding of SiOC etch mechanism and the transition of etch behavior from SiOC to poly-Si can inform us on the appropriate etch regime to optimize SiOC etch and poly-Si protection.

In this work, we examine SiOC etch both isotropically and anisotropically using an inductively coupled plasma (ICP) chamber. We investigate CF_4/O_2 isotropic etch on the stacked samples by varying the CF_4/ O_2 ratio and study its effect on the composition of modified layer and SiOC-to-poly-Si transition by combining *in-situ* ellipsometry and post-process vacuum-transferred XPS. *Ex-situ* AFM and SEM measurements will be provided to understand the surface roughening process as well.

Our study shows that during the CF_4/O_2 isotropic etch of ~25 nm SiOC/poly-Si stack a etch transition from SiOC etching to poly-Si etching after~13 nm of SiOC is removed and the remaining 12 nm of “SiOC” becomes highly modified . One possible interpretation of this early poly-Si transition is that carbon composition can be removed quickly compared to the overall SiOC etch rate which creates a carbon-deficient porous modified top layer. This modified layer allows for an earlier poly-Si isotropic etch once it is fully porous. During poly-Si etch, the porous layer remains on the poly-Si while a transitioning SiO_xF_y interfacial layer is being formed on the poly-Si. Consistent with expectations, XPS surface analysis shows a steady decrease in C-Si and C-C/H bonding of SiOC with progressive plasma treatment.

With a better understanding of the etch mechanism, additional experimental results with varying precursor type (HFC vs FC), plasma power, bias voltages, and material carbon concentration will be presented to demonstrate optimal etch regimes for SiOC to poly-Si selectivity. In addition to planar etch of these substrates, aspect ratio dependent etch (ARDE) of SiOC will be discussed using trench structures[1].

1. Chung, S.-J., Luan, P., Park, M., Metz, A., & Oehrlein, G. S. Exploring oxide-nitride-oxide scalloping behavior with small gap structure and chemical analysis after fluorocarbon or hydrofluorocarbon plasma processing. *J. Vac. Sci. Technol. B* 41, 062201 (2023).

11:00am **AS-WeM-13 Multimodal Surface Analysis and Depth Profiling Using Femtosecond Laser Ablation, Ion Sputtering, and Ion Scattering Spectroscopy***, **Paul Mack**,* Thermo Fisher Scientific, UK

Recent advances in surface and interface analysis are enabling new approaches for characterizing complex materials. The Thermo Scientific™ Hypulse™ XPS system combines X-ray Photoelectron Spectroscopy (XPS), Ion Scattering Spectroscopy (ISS), monatomic and gas cluster ion sputtering, and femtosecond laser ablation within a single platform, allowing characterization across length scales ranging from the outermost atomic layer to buried interfaces tens of microns below the surface.

At the very top surface, Ion Scattering Spectroscopy (ISS) will be used to examine the surface coverage of oxidized tungsten-containing layers on Ni-rich NMC battery powders, demonstrating the ability to distinguish between partial and complete surface coverage with true monolayer sensitivity. This presentation will then demonstrate the use of femtosecond laser ablation for extending XPS depth profiling into regimes inaccessible using conventional sputtering approaches. Example applications will include rapid profiling through thick graphitic battery anode structures (~25 µm), enabling characterization of compositional and chemical variations throughout porous electrode materials and buried interphases. In addition, femtosecond laser-based cleaning and shallow profiling of a thin film material will be presented, illustrating preservation of the characteristic XPS chemical structure during surface preparation compared to conventional sputtering methods.

A combined multimodal depth profiling methodology based on sequential MAGCIS ion sputtering and femtosecond laser ablation will also be described. This approach enables depth profiling of chemically sensitive oxide materials such as HfO_2, Ta_2O_5, and TiO_2 with substantially reduced chemical damage compared to conventional ion sputtering alone. The preservation of characteristic metal oxide spectral features and near-correct oxide stoichiometry during profiling will be discussed.

These examples illustrate how complementary surface analysis and depth profiling methods can be applied across very different length scales and materials systems. The combination of ISS, gas cluster sputtering, and femtosecond laser ablation enables comparison of outermost surface composition, near-surface chemistry, and deeper buried structures within the same experimental workflow. Particular emphasis will be placed on the preservation of chemically sensitive species during cleaning and profiling, and on extending XPS analysis to thicker and more structurally complex materials than are typically accessible using conventional sputtering methods.

11:15am **AS-WeM-14 Velocity-Resolved Snms as a Surface-Analytical Probe of Electronically Driven Sputtering Under Swift-Heavy-Ion Irradiation***, **Lars Breuer**, Tobias Heckhoff,* University of Duisburg-Essen, Germany*; Frieder Koch,* GSI Helmholtzzentrum fuer Schwerionenforschung, Germany*; Marika Schleberger, Andreas Wucher,* University of Duisburg-Essen, Germany

Sputtering under keV ion bombardment is commonly described by nuclear collision cascades, while sputtering under swift-heavy-ion (SHI) irradiation is driven by electronic excitation and the subsequent conversion of deposited energy into atomic motion. This different energy-conversion pathway leads to altered sputtering characteristics, such as ionization probabilities and velocity distributions of sputtered material. Accessing such velocity distributions experimentally is challenging because SHI beams at accelerator facilities are often quasi-continuous and therefore not directly compatible with conventional pulsed ToF-SIMS/SNMS schemes.

Here, we use velocity-resolved secondary neutral mass spectrometry (SNMS) to probe neutral-particle emission from surfaces under nuclear- and electronic-stopping conditions on a common experimental basis. The approach combines laser post-ionization with a laser-delay scheme, in which the delay between the ionizing laser pulse and pulsed extraction into a time-of-flight mass spectrometer is varied. In contrast to classical extraction-delay methods, the timing reference is set by the post-ionization laser rather than by a short primary-ion pulse. The method is therefore applicable to quasi-continuous SHI beams, such as those available at GSI, while retaining sensitivity to the velocity distribution of sputtered neutral species.

Velocity distributions were measured for representative target materials, including indium, bismuth, and sodium chloride. Collision-cascade sputtering was investigated using 5 keV Ar^+ bombardment, whereas electronically driven sputtering was probed with 4.8 MeV/u $^{48}Ca^{10+/19+}$ and $^{197}Au^{26+/54+}$ projectiles quasi simultaneously. For all investigated targets, SHI-induced emission shows a pronounced shift toward lower velocities compared with the keV reference case. This finding demonstrates that electronically driven sputtering cannot be treated as a straightforward extension of nuclear collision cascades. At the same time, the distributions are not reproduced by a simple Maxwell-Boltzmann description, indicating that the emission is not governed by a purely thermal evaporation-like process.

These results establish laser-delay-based, velocity-resolved SNMS as a surface-analytical probe of energy conversion and particle emission under electronic-stopping conditions, providing mechanistic insight into SHI-induced sputtering.

11:30am **AS-WeM-15 Experimental Validation of Monte Carlo Transport Simulations for MoS_2 Sputter Deposition***, **Alexander Mings**, Kyle Dorman, Steven Larson, Tomas Babuska, John Curry, David Adams,* Sandia National Laboratories

Sputter-deposited MoS_2 coatings are widely used in aerospace applications because they provide reliable solid lubrication and ultralow friction in vacuum. However, their layered structure often promotes porous film growth, reducing wear life and increasing susceptibility to oxidation. Process optimization to improve film density is typically empirical, costly, and difficult to transfer between deposition systems. Monte Carlo transport simulations have demonstrated success in streamlining this process, but their reliability depends heavily on experimental validation.

In this work, SRIM and SIMTRA are used to model the transport of sputtered atoms and backscattered neutrals during MoS_2 deposition. Key simulation outputs are validated experimentally at the substrate using a pinhole camera to measure the angular distribution of sputtered species, and wavelength-dispersive spectroscopy (WDS) to map spatial variations in sulfur flux. To indirectly assess post-ionized backscattered neutrals, a retarding field energy analyzer (RFEA) is used to measure the ion flux and energy distributions. Film hardness is further used as a proxy for porosity to connect deposition conditions with coating densification. This work assesses the extent to which Monte Carlo simulations can predict the flux conditions that produce dense MoS_2 coatings and provides a framework for more efficient process development and transfer.

Sandia National Laboratories is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.

11:45am **AS-WeM-16 TOF-SIMS Depth Profiling of Inorganic–Organic Multilayers Using a Hybrid Sputtering Approach***, **Shin-ichi IIDA**,* ULVAC-PHI, Japan*; Jacob Schmidt,* Physical Electronics*; Gabriele Di Stadio,* ULVAC-PHI, Italy

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) combined with argon gas cluster ion beam (Ar-GCIB) sputtering is widely used for low-damage depth profiling of organic materials. However, the extremely low sputtering yield of Ar-GCIB for inorganic materials remains a major limitation for the analysis of inorganic–organic multilayer systems. To address this challenge, a hybrid sputtering approach combining low-energy Cs^+ ions and Ar-GCIB was applied to TOF-SIMS depth profiling of inorganic–organic multilayer structures. Periodic multilayer samples consisting of Al interlayers embedded within micrometer-thick Irganox 1010 films were prepared as a model system. Depth profiling was performed using combined Cs^+ and Ar-GCIB sputtering. The hybrid sputtering conditions enabled efficient removal of buried Al layers while preserving characteristic molecular ion signals from Irganox 1010 over extended sputter depths. The results demonstrate that hybrid Cs^+/Ar-GCIB sputtering enables reliable TOF-SIMS depth profiling of inorganic–organic multilayer systems while maintaining molecular information throughout the analysis.

12:00pm **AS-WeM-17 Resolving Chemical Speciation in Complex Nickel-Based Electrocatalysts through Detailed XPS Analysis and Corroborations with ToF-SIMS***, **Emilia McCann**,* Colorado School of Mines*; Doha M. Sayed,* Los Alamos National Laboratory*; Virginia Larson, Meital Shviro,* National Laboratory of the Rockies*; Luigi Osmieri, Piotr Zelenay,* Los Alamos National Laboratory*; Svitlana Pylypenko,* Colorado School of Mines

X-ray photoelectron spectroscopy (XPS) is essential for characterizing nickel-based electrocatalysts, however the Ni 2p region is notoriously challenging due to overlapping peaks, complex satellites and spectral similarities between different oxidation states and chemical environments. This complexity intensifies in complex catalysts where nickel coexists with another metal such as iron or molybdenum and/or is present in the form of phosphides or carbides, in addition to oxides and hydroxides. These various chemistries are widely explored for catalyzing reactions in liquid alkaline water electrolyzers (AWE) and anion-exchange membrane water electrolyzers (AEMWEs), yet poorly characterized and reported in the literature. In this work, a series of Ni-containing electrocatalysts, including pristine and tested iron-doped NiOx , NiMo, NiPx, and NiMoPx supported on Ni substrate (either Ni foam or Ni fiber), were examined using XPS to track differences in nickel surface composition. The approach to deconvoluting Ni 2p XPS spectra is built on established fitting parameters for nickel oxides, hydroxides and mixed iron-nickel compounds [1]. Additional fitting parameters were systematically developed to include mixed Ni, Mo, P, O species, including NiOOH-MoO4, NiMoO4, NixPy and NiPO4, using reference samples, while complementary analysis of the Fe 2p, Mo 3d and P 2p spectral regions was conducted to more effectively capture trends in nickel speciation. Each species is characterized by specific binding energies, full width at half-maximum (FWHM) values, satellite positions and asymmetric line shapes necessary to accurately deconvolute XPS spectra. Additionally, this work used ToF-SIMS to analyze selected samples with the goal of identifying certain relevant molecular fragments. The strong correlation between XPS-derived compositions and ToF-SIMS molecular fragments representing certain species, including NiOOH-, MoO4-, PO4-, NiP+ and NiPO4- species, validated the detailed XPS fitting approach presented here. These results provide a set of fitting parameters for complex nickel systems, demonstrating that rigorous multi-technique characterization can resolve ambiguities in transition metal XPS analysis assisting further electrocatalyst optimization for various electrochemical systems. AcknowledgementFinancial support for this work was provided by the U.S. DOE, Critical Materials and Energy Innovation (CMEI)/Alternative Fuels and Feedstocks Office via Electrocatalysis Consortium (ElectroCat)

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.

Applied Surface Science
Room 321 - Session AS-ThM

Complex Data Analysis For Applied Surface Science

Moderators: Dr. Jonathan Counsell, Kratos Analytical Inc, **Dr. Jeffrey Terry**, Illinois Institute of Technology

11:00am **AS-ThM-13 Data-Driven Analysis Using Explainable AI (XAI) for Surface Analysis Data, Including Mass Images**, ***Satoka Aoyagi,*** Seikei University, Japan **INVITED**

Sophisticated analysis methods, such as secondary ion mass spectrometry, provide rich information about a sample, from which we could generally extract and interpret only a part of it. The effective application of machine learning methods to such data is useful for extracting hidden yet important information with which to characterize the sample. Although there are a variety of methods to analyze complex datasets, the methods that also provide the information on the analysis processes are crucial for analyzing scientific data. This presentation focuses on such methods, known as explainable AI (XAI). Unsupervised learning methods, such as principal component analysis (PCA), non-negative matrix factorization (NMF) and autoencoder (AE), are useful for understanding the outline of the data and sample that are analyzed. Supervised learning methods are powerful for further analysis, such as exploring related factors of a particular material or characteristic in a sample. Combining unsupervised and supervised learning methods provides detailed information on related variables, such as groups of mass peaks from the same material, and on the relationships between particular sample conditions and chemical structures. The application of unsupervised learning methods, such as PCA, NMF and AE, and supervised learning methods, such as artificial neural network (ANN)-based methods [1-3] and Random Forest [4], to organic complex sample datasets is introduced. Moreover, ANN-based systems are useful in dealing with datasets including non-linear factors such as matrix effects, which cause peak intensity changes regardless of the concentration of a target material. The weights of ANN systems indicate which variables are important for the purpose of the analysis, suggesting whether an ANN system outputs answers depending on the appropriate variables. For example, quantitative analysis including interface evaluation of multilayers in depth profiles often requires correction methods. ANN is generally powerful for the ANN-based system developed for secondary ion mass spectrometry (SIMS) data of three-component systems, which is introduced here.

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[3] S. Aoyagi et al., *Anal. Chem*., **95**(40), 15078-15085 [tel:15078-15085] (2023).

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11:30am **AS-ThM-15 Data-Driven Automation for X-Ray Photoelectron Spectroscopy (XPS)**, ***David Valley***, *James Johns, Jiayue Lin, Jennifer Mann, Kateryna Artyushkova,* Physical Electronics

We are presenting a set of data-driven tools aimed at simplifying XPS analysis while using data-driven decision making processes to maintain flexibility for advanced use. The approach uses both machine learning and analytical models to automate key steps in both sample setup and data acquisition.

In XPS analysis, typically samples are small, or cut to a smaller size to accommodate the instrument. As a result, multiple samples will fit on a sample holder (platen) and in a high throughput instrument, multiple sample holders can be put in the instrument at once, resulting in potentially 100s of samples in the instrument at any given time.XPS users have identified pain points of the repetitive, tedious work of creating analysis points on each sample mounted on the platen. To address this necessary, but time-consuming step usually performed by the user, we have developed three machine learning models to automatically detect the platen type, platen-photo alignment, and the sample locations on the platen. These are used to automatically qualify the platen upon introduction to the instrument and populate potential analysis positions.

A second set of tools is to use statistical methods to optimize the basic analysis routines that are the starting point for XPS analysis. XPS analysis requires the acquisition of a wide energy range survey spectrum to identify the elements on the surface of the sample, followed by narrow scans that focus on the elements of interest to get higher signal-to-noise for quantification purposes and/or reveal the chemical state of a particular element. We introduce a data-based optimization routine to determine the time balance to get the best data quality for the region acquisitions scans based on a measurement of the survey scan. From the signal-to-noise of the equal time-based survey acquisition we extrapolate the expected error in the atomic percent quantification and choose optimum routines. The optimum is not a unitary choice and there is a pareto optimal front of possible acquisitions states. Based on user input we create an objective function which fits the user's desire for the acquisition result.

11:45am **AS-ThM-16 Computational Assessment of Environment-Dependent Mineral Surface Transformations**, ***Jennifer Bjorklund***, *Sara Mason,* Center for Functional Nanomaterials, BNL

Understanding how mineral surfaces evolve and react under environmentally-relevant conditions is crucial to predicting interfacial processes governing resource recovery, nutrient cycling, and aqueous geochemistry. Minerals like pyrite (FeS_2) and struvite ($NH_4MgPO_4 \cdot 6H_2O$) are environmentally and technologically important systems whose surface chemistry is sensitive to aqueous conditions, with reactivity ultimately controlled by termination, hydration, protonation state, and local atomic configuration. Here, using an approach that combines Density Functional Theory (DFT) calculations with atomistic thermodynamics, we characterize surface stability, transformation pathways, and their impact on reactivity under relevant chemical conditions.

For pyrite, we explicitly compare hydroxylation and protonation of exposed surface sites to determine stable interfacial configurations as a function of aqueous conditions (pH, temperature, pressure). We further assess possible modes and energetics of arsenic (As) incorporation into near-surface and surface sites, identifying preferred structural motifs and their influence on local electronic structure. Building on these structural models, we evaluate gold (Au) adsorption energetics to understand how environmentally induced surface transformations and dopant incorporation modify interfacial binding and reactivity relevant to gold deposition and ore formation processes.

For struvite, we investigate pH-dependent stability of multiple surface terminations derived from the underlying bulk composition, explicitly sampling variations in protonation and hydration states. By constructing thermodynamic comparisons of these stable configurations, we identify dominant surface structures under varying aqueous conditions and quantify how protonation and hydration influence stability and reactivity. These results provide molecular-level insight into the transformations of struvite surfaces under realistic environmental conditions associated with nutrient release.

Together, these insights highlight how aqueous conditions drive surface transformations in mineral systems and how these transformations control downstream interfacial reactivity. By linking surface stability, protonation/hydration, dopant incorporation, and adsorption energetics, this work provides a unified framework for understanding environmentally-relevant responsible mineral interfaces at the atomic scale.

12:00pm **AS-ThM-17 Surface and Subsurface Chemistry of IrOx Electrocatalysts: A Multi–Technique Approach Integrating ToF–SIMS, XPS, and Multivariate Analysis**, ***Lonneke van Eijk***, Colorado School of Mines, USA*; Genevieve Stelmacovich,* LAM Research*; Michael Walker,* Colorado School of Mines, USA*; Rebecca Hamlyn,* Lawrence Berkeley Lab, USA*; Zhao Li, Xiaoping Wang,* Argonne National Laboratory, USA*; Ethan Crumlin,* Lawrence Berkeley Lab, USA*; Alexey Serov,* Oak Ridge National Laboratory, USA*; Deborah Myers,* Argonne National Laboratory, USA*; Svitlana Pylypenko,* Colorado School of Mines, USA

Understanding the surface and subsurface chemistry of IrO_x electrocatalysts is essential for advancing performance of Proton Exchange Membrane Water Electrolyzers (PEMWEs). Commercial IrO_x powders exhibit diverse physicochemical properties and the interplay between various properties and activity and stability is still under investigation. In this work, six commercial IrO_x catalysts were examined. Initial studies used a suite of characterization methods including bulk structural and compositional techniques such as XRD, PDF, SAXS/USAXS, and XAS, as well as surface sensitive structural and compositional methods BET surface area analysis and XPS. These measurements were combined with electrochemical properties, including electrical conductivity and electrochemical measurements in rotating disk electrode configuration to assess activity and stability. This work also includes analysis of the same set of samples with ToF–SIMS, to further access surface and near-surface chemical information, extending into the bulk through depth profiling, to corroborate

and complement other methods. This is accomplished using a three–stage framework for interpreting IrO_x surface chemistry using PCA.

First, ToF–SIMS is examined independently to determine how fragment distributions, depth–dependent signals, evaluated in the context of matrix effects to understand how they correlate with IrO_x composition, oxygen environments, and defect-related chemistry. This step clarifies how ToF–SIMS can be reliably applied to complex oxide electrocatalysts and what chemical information it uniquely provides. Second, ToF–SIMS results are correlated with XPS to refine chemical-state assignments. ToF–SIMS fragment trends are used to validate or challenge XPS peak-fitting models, improving confidence in oxidation-state and oxygen-species interpretation. Finally, ToF–SIMS and XPS parameters are correlated to bulk compositional and structural parameters along with electrochemical metrics. PCA reveals cross–technique correlations that reveal how surface chemistry and subsurface structure relate to catalyst performance and robustness. By combining complementary vacuum–based methods with statistical analysis, this work demonstrates how multi–characterization strategies resolve ambiguities that cannot be addressed by any single technique. The resulting framework provides a generalizable approach for using ToF–SIMS and XPS together to interrogate complex oxide surfaces and highlights the power of integrated surface analysis for understanding structure–chemistry relationships in advanced electrocatalysts.

Advances in Battery Engineering, Interface Design, and Characterization Mini-Symposium
Room 319 - Session BT1+AS+CA+TF-ThM

Interface Engineering in Batteries

Moderators: Prof. Dr. Adriana Creatore, Eindhoven University of Technology, **Prof. Alexander Kozen**, University of Vermont

8:00am **BT1+AS+CA+TF-ThM-1 Plasma and Electrochemical Modification of Battery Cathode Surfaces to Enhance Voltage Stability and Thus Energy Density***, **Paul Braun,*** University of Illinois Urbana-Champaign **INVITED**

The energy density of battery cathodes increases dramatically with increases in voltage. However, higher operating voltages, in particular above 4.3V leads to significant capacity degradation. Because the mechanism of capacity degradation is often a surface-initiated reaction, modification of the exposed surface of the cathode material is a promising approach to increase energy density without adding significant mass or volume to the battery. Two approaches we are investigating to increase the voltage stability of $LiCOO_2$, a common battery cathode material, include surface modification via a plasma process, and electrochemical deposition of a high voltage stable material. Both methods result in a thin layer of high voltage stable material on the surface of the active cathode material. The plasma modification forms a nanoscale layer of disordered rocksalt on the underlying layered $LiCoO_2$ while the electrochemical modification grows a layer of lithiated manganese oxide on the underlying $LiCoO_2$. In both cases, the cyclable energy density of the $LiCoO_2$ is increased significantly.

8:30am **BT1+AS+CA+TF-ThM-3 Interfacial Engineering of Battery Materials using Atomic Layer Deposition***, **Neil Dasgupta,*** University of Michigan, Ann Arbor **INVITED**

Interfaces and interphases play a critical role in battery performance, both in current state-of-the-art Li-ion batteries (LIBs), as well as next generation battery technologies. Therefore, there are great efforts to understand, control, and improve the properties of battery interfaces and interphases. This quickly becomes a multi-dimensional optimization problem, where the required properties of interfaces span from performance (i.e. fast rate capability), stability (i.e. long calendar life) and compatibility with the adjacent chemical and material phases. To address these challenges, there has been increasing interest in the application of 'artificial interphase' layers, which are typically comprised of nanoscale thin-film coatings along electrode-electrolyte interfaces. From a manufacturing perspective, it is critical that these surface coatings be deposited in a conformal, reproducible, scalable, and low-cost manner.

Towards these goals, our research group has developed a range of surface coating layers for battery applications, both for LIBs with liquid electrolytes, as well as next-generation systems such as Li metal anodes and solid-state batteries. In this talk, I will summarize recent progress towards precise and tunable interfacial control in batteries with both liquid and solid electrolytes, using atomic layer deposition (ALD) as an enabling platform. I will describe the development of advanced ALD chemistries, beyond the binary oxide systems that are typically employed. In LIBs, I will describe how surface coatings can simultaneously enable low-temperature and fast charging of graphite anodes without Li plating. In solid-state battery systems, I will describe the stabilization of cathode/solid electrolyte interfaces, enabling high-voltage cycling above 4.5 V. Finally, I will describe our efforts towards scalable manufacturing of ALD-coated battery electrodes, through the development of atmospheric-pressure spatial ALD technologies.

9:00am **BT1+AS+CA+TF-ThM-5 Atomic Layer Deposition (ALD) Tuned Interfaces for High-Performance Lithium- and Manganese-Rich Cathodes***, **Jahnavi Manikantan Sudharma,*** Argonne National Laboratory*; Jeffrey Elam,* Argonne National Laboratory, USA

The growing deployment of renewable energy and the rapid expansion of artificial intelligence and machine learning infrastructures place increasingly dynamic demands on modern electrical grids, requiring the need for high-performance, renewable energy-storage technologies. While nickel (Ni)-rich layered oxides remain the state-of-the-art materials for lithium-ion battery cathodes, their reliance on costly and supply-constrained Ni and cobalt (Co), motivates the development of alternative materials. Lithium- and manganese (Mn)-rich (LMR) cathodes offer a compelling solution due to their high energy density and reversible capacities enabled by anionic redox. However, oxygen loss associated with this redox process induces severe surface and interfacial degradation, including electrolyte decomposition, transition-metal migration, and Mn dissolution, which hinder long-term cycling stability of these cathodes. Suppressing Mn dissolution at the surface is still a key challenge. Advancing surface engineering, structural tuning, and electrolyte optimization is therefore critical to unlocking the full potential of LMR cathodes for next-generation energy-storage systems. Atomic layer deposition (ALD) being a self-limiting thin film growth method characterized by the sequential exposure of chemical species, offers a promising strategy to stabilize the interfaces by depositing tailored ultrathin, uniform and conformal coating layers on the surface and thereby mitigating the surface degradation of the cathode. Surface coatings applied through atomic layer deposition (ALD) offer a highly controlled route to stabilize these interfaces; however, the fundamental mechanisms governing how different ALD chemistries interact with LMR surfaces remain poorly understood. In this presentation, I will discuss our recent study combining in situ measurements of ALD chemistries, ex situ thin film characterization, and electrochemical testing of prototype batteries. By systematically investigating ALD coating chemistries including lithium phosphate (Li_3PO_4) and lithium borate ($LiBO_x$), we elucidated how ALD surface reactions govern coating composition, structure, and protective functionality and how this functionality affects cycling performance. These insights will inform rational interface-engineering strategies, enabling the practical deployment of high-energy, cobalt-lean Mn-rich cathodes for next-generation lithium-ion batteries.

9:15am **BT1+AS+CA+TF-ThM-6 Atomic Layer Deposition for Lithium Metal Anode Stability***, Niels Hoogedoorn, Meike Pieters, Cristian van Helvoirt, **Mariadriana Creatore,*** Eindhoven University of Technology, Netherlands

High-performance lithium-ion batteries (LIBs) are hampered by phenomena such as dendrite growth, electrolyte decomposition and uncontrolled interface formation between electrode and electrolyte. This is especially the case of next-generation battery materials, such as Si-anodes, Li-metal anodes and solid-state electrolytes. To address these challenges, atomic layer deposition (ALD) offers a promising pathway by engineering ultrathin conformal interfacial layers with atomic-scale precision.

In this contribution we present our recent work on ALD processes on lithium metal anodes (LMAs). The studies include: Al_2O_3, LiPO, LiPON and LiF, all developed in a FlexAL ALD-reactor (Oxford instruments). The supercycle approach for the process development of LiPO is highlighted: a novel Li-precursor, Lider™, is combined with an oxygen plasma (O_2*) and trimethyl phosphate (TMPO). The films are free of carbon impurities, despite that, during the subcycle of Lider + O_2*, Li_2CO_3 is detected by XPS in combination with a vacuum transfer unit. We find that a chemical vapour transformation [1] occurs, where the subsequent exposure of Li_2CO_3 to TMPO, leads to the abstraction of carbonate from the film, towards C-free LiPO [2].

Additionally, we discuss the deposition of these ALD layers on LMAs and their effect on the critical current density (CCD) of the LMAs, tested in a Li | argyrodite | Li symmetric cell. A home- built vacuum transfer module is used to transport the LMAs between a glovebox and the ALD reactor, where the ALD layers are processed at 120 °C. The CCD is the maximum electrical current per unit area that the anode can withstand before

reaching failure, typically caused by lithium dendrite induced shorting. Depending on the material, and layer thickness, the ALD layers improve the CCD by more than 40%. For example, in the case of 10 Al_2O_3 cycles, the maximum sustainable current density increases from 2.4 mA/cm^2 to 3.4 mA/cm^2, thereby demonstrating enhanced stability against dendrite shorting. These results illustrate how engineering ALD interface layers can improve the CCD of LMAs and mitigate challenges in LMA stability. Moreover, these studies propose CCD measurements as screening approach of ALD chemistry and processing conditions towards their implementation and testing in full LIB cells.

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9:30am **BT1+AS+CA+TF-ThM-7 Buffer Layer Oxidative Polymerization to Stabilize Li Metal Anodes for Lithium Ion Batteries***, Amit K. Datta, Blaine D. Kelly, Dilan M. Gamachchi, Indeewari M. Karunarathne, Campbell A. Sweet, Andrew C. Meng, Matthias J. Young,* University of Missouri

Li metal anodes promise an order of magnitude higher energy density than conventional graphite anodes in Li ion batteries, however, the practical use of Li metal as an anode remains limited by several factors such as unstable interfacial reactions, continuous electrolyte decomposition, and dendritic Li growth, leading to rapid cell failure. Oxidative Molecular Layer deposition (oMLD) offers the ability to deliver thin film polymer coatings with electronic, ionic and chemical properties of interest for improving stability of Li metal anodes, but oMLD employs harsh oxidants that are not compatible with Li metal substrates. In this work, we demonstrate an approach we term buffer layer oxidative polymerization (BLOP), to enable the delivery of oMLD coatings onto Li metal. We investigate three BLOP derived polymer coatings on Li metal: polyhydroquinone (pHQ), poly(2,5-dimercapto-1,3,4-thiadiazole) (pDMCT), and poly(p-phenylenediamine) (pPDA). These three coatings were selected as representative classes of coatings based on their electronic and ionic conductivity differences: pHQ exhibits both Li ion conductivity and electronic semiconductivity, pDMCT shows only Li ion conductivity and pPDA shows anionic conductivity and electronic semiconductivity. Galvanostatic charge-discharge measurements in Li-Li symmetric cells show differences in the stability enhancement among the different coatings, with a clear benefit for BLOP vs. oMLD and MLD. Electron microscopy on these coatings helps understand the crosslinking depth achieved from BLOP coatings generated by different organic monomers. Overall, this work demonstrates the oxidative synthesis of multiple polymeric thin films directly on Li metal without degrading the substrate and identifies that coatings with Li ion conductivity and electronic semiconductivity show improved Li metal stability over the alternatives.

9:45am **BT1+AS+CA+TF-ThM-8 Modulation of Anode-Free Sodium Battery Interfaces through Atomic Layer Deposition of NaF***, Jonathan Thurston, Aaron Melemed, Neil Dasgupta,* University of Michigan

Sodium-based batteries are a promising alternative to lithium-ion technologies due to the higher earth abundance and lower cost of sodium. Furthermore, when Na metal electrodes are used in an “anode-free” configuration, the theoretical energy density is competitive with that of lithium-ion systems. However, the effects of the current-collector surface chemistry on the subsequent Na plating/stripping and solid electrolyte interphase (SEI) composition remains limited.

In this study, we synthesize an “artificial SEI” of NaF using atomic layer deposition onto the surface of Cu current collectors (CCs). Thermal ALD of NaF is successfully demonstrated using sodium *tert*-butoxide and ammonium fluoride precursors. We investigate the impact of the NaF surface layers on the subsequent morphology of deposited sodium using electron microscopy. A multi-modal suite of near-edge X-ray absorption spectroscopy (NEXAFS), X-ray photoelectron spectroscopy (XPS), and infrared spectroscopy (IR) are used to characterize the composition and structure of the resulting SEI as a function of depth and battery cycling. Our results show that the NaF layer encourages more homogenous plating with controlled nucleation sites, while bare Cu CCs have more sporadic nucleation sites for Na metal and a more dendritic mossy plating morphology. Additionally, electrochemical impedance spectroscopy (EIS) and chemical state identification indicate that a more stable SEI is formed in the first few cycles for NaF-coated Cu CCs, while an evolving SEI is observed for uncoated Cu CCs. Our work demonstrates the importance of surface layers in anode-free battery current collectors, while investigating the dynamic nature of the SEI composition and structure throughout cycling.

Advances in Battery Engineering, Interface Design, and Characterization Mini-Symposium
Room 319 - Session BT2+AS+CA+TF-ThM

Advanced Battery Electrodes

Moderators: Prof. Alexander Kozen, University of Vermont, **Dr. Tanguy Terlier**, Rice University, **Dr. Andrew Westover**, Oak Ridge National Laboratory

11:00am **BT2+AS+CA+TF-ThM-13 Understanding the Electrically-Limited Reaction Kinetics and Dynamics for Conversion Electrode Iron Fluoride***, Chuan-Fu Lin,* Catholic University of America **INVITED**

To maintain efficient reaction kinetics in standard electrodes, fast and stable ionic and electronic conductive networks are required for long-term reversibility, and this poses the major challenges for conversion-type electrode materials. The phase separation reaction, CM + Li^+ + e^- -> M (reduced metal) + LiX (Li compounds), induced by the lithiation process deteriorates the structural integrity, which certainly destroys the original ionic and electronic pathways and reconstructs new ones. However, it is still unclear whether the transports of conversion electrode are benefited or hindered from the reconstruction of transport pathways due to phase separation, yet the dynamic evolution of electrical conductivity in these systems remains overlooked.

This work aims to investigate the electrically-limited reaction of conversion electrodes upon phase separation and recombination by studying the structural, electrical, and electrochemical properties of amorphous and crystalline iron (III) fluoride (FeF_x) thin films synthesized via sputtering deposition. Using a binder-free lateral device architecture and probing measurement, we dynamically mapped resistivity evolution during electrochemical cycling. While pristine crystalline films exhibit lower initial resistivity than amorphous films, deep lithiation triggers a dramatic drop in resistivity by over five orders of magnitude in both structural variants. Despite the massive volume fraction of the insulating LiF byproduct (1 : 4.17 for Fe : LiF ratio), the resistivity reduced to ~0.35 Ω·m, demonstrating a common conduction pathway formed by a metallic Fe network within the nanocomposite. Correlating this resistivity evolution with X-ray Photoelectron Spectroscopy (XPS) spectra reveals the electrically-controlled reaction dynamics of the thin-film conversion electrodes. Conversely, delithiation results in a resistivity increase of two orders of magnitude, driven by a rate-dependent electrochemical "trapping effect." Fast charging causes isolated Fe domains electronically stranded within the LiF matrix and driving irreversible capacity loss. These results elucidate the coupling between chemical quantifications, reaction dynamics, and electrical properties, providing understanding of the influence of the electrical conductivity for high-energy-density conversion cathodes.

11:30am **BT2+AS+CA+TF-ThM-15 Correlating Electrical Property Evolution and Reversibility in Sputtered ZnO Thin-Film Conversion Electrodes***, Sukanya Goswami, Chuan-Fu Lin,* The Catholic University of America

During conversion reaction in Lithium-ion batteries, electrical properties shift as reaction kinetics vary with phase separation, state of charge, and evolving conductivity. Understanding how these dynamic electrical transitions govern reaction control is essential for optimizing conversion electrodes. This study probes the evolution of ZnO conversion electrodes during cycling, examining the electron transport, reversibility and capacity retention. Because the literature on ZnO remains limited, it provides a simple benchmark for testing broader conversion-mechanism concepts and for comparing phase separation and recombination process across conversion materials in LiBs. **Sputter-deposited ZnO thin films** were cycled in a lithium-ion half-cell configuration and their electrical transport properties tracked ex-situ using **two-probe resistivity measurements** after each set of cycles.

The resistivity data reveal a clear and progressive deterioration in electronic transport over cycling. Starting from values on the order of **10^{-4} Ω.m** in the early cycles, resistivity increases by several orders of magnitude, reaching **1-7 Ω.m** by **cycle 30**. This monotonic rise reflects a gradual breakdown of the conductive percolation network as the conversion reaction proceeds. Persistent differences in resistivity during early cycling reveal an asymmetry between lithiation and delithiation, likely caused by sluggish reconversion kinetics of the phase-separated products. These electrical changes correlate directly with coulombic efficiency. When the electrode maintains sufficient conductivity, capacity retention is upto **95%**. Conversely, as resistivity rises sharply with progressive cycling, coulombic efficiency becomes irregular and drops. This correlation implicates degradation of electronic transport,

driven by delamination caused by the volume expansion during phase transformation, as the primary mechanism governing capacity fades.

To understand the structural and chemical origins of these changes, cycled electrodes were characterized by **XRD, XPS, and SEM**. XRD tracked phase separation and recombination between ZnO, metallic Zn and Li_2O. XPS provided insight into surface chemical states and irreversible interfacial species, while SEM captured morphological degradation including delamination. Together, these results establish a direct link between electronic conductivity, conversion reaction reversibility and coulombic efficiency, offering a framework for mitigating kinetic limitations in ZnO based thin film cathodes.

11:45am **BT2+AS+CA+TF-ThM-16 Molecular Mapping Investigations of Prelithiation Alloy Formation via Thermal Evaporation on Silicon Based Electrodes***, **Gabriel Parker**, Amanda Musgrove, Gabriel Veith, Ivan Matyushov, Xiao-Ying Yu,* Oak Ridge National Laboratory, USA

Abstract: Silicon based composites have become increasingly popular as potential anodes for lithium-ion batteries due to their large storage capacity, relative abundance, and low cost. However, these anodes often see reduced initial columbic efficiency (ICE) due to disruptive volume expansion up to 300% and continuous unstable solid electrolyte interphase (SEI) layer formation. Prelithiation, the process of adding excess reservoir of Li to the electrode to compensate for irreversible SEI formation losses during their sample preparation, has proven to solve the issue of immediate capacity loss. Thermal evaporation is a prelithiation technique with limited studies on its effectiveness. In this study, time-of-flight secondary ion mass spectrometry (ToF-SIMS) is used to investigate the benefits of prelithiation via thermal evaporation. ToF-SIMS provides chemical mapping and spatial information in 2D and 3D visualizing the deposition of lithium, identifying Li_xSi_y alloy and $Li_xSi_yO_z$ silicate formation, and the distribution of lithium passivation into the electrodes. Passivation under different atmospheric conditions, such as inert Argon (Ar) and Ar/carbon dioxide (CO_2), highlights the impact of the environment on the passivation effectiveness and formation of Li_xSi_y alloy and $Li_xSi_yO_z$ silicate. The ToF-SIMS molecular imaging and depth profiling results indicate that prelithiation via thermal evaporation effectively distributes lithium throughout the depth profile thickness of several hundred nanometers. It induces a greater degree of $Li_xSi_yO_z$ silicate formation over Li_xSi_y alloy. The results provided by the ToF-SIMS are corroborated by electrochemical measurement of the electrodes under inert Ar and Ar/CO_2 environments indicating that the Ar/CO_2 electrode retained a higher specific capacity over multiple cycles. Our ToF-SIMS characterization results show the effectiveness of thermal evaporation in producing a more stable electrode and an electrode with an effective lithium reserve that can preserve its capacity.

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

12:00pm **BT2+AS+CA+TF-ThM-17 Engineering Conformality of Lithium–Terephthalate Thin Films via Precursor Selection***, **Anish Philip**, Joakim Jestilä, Milad Madadi,* Aalto University, Finland*; Jussi Kinnunen,* Chipmetrics Ltd, Finland*; Antti Karttunen, Maarit Karppinen,* Aalto University, Finland

Lithium-terephthalate (Li-TP) is recognized as a highly promising anode material for lithium-ion batteries.[1] The advantages of atomic/molecular layer deposition (ALD/MLD) technique have enabled the realization of Li-TP thin films in a highly controllable manner needed for its use in thin-film microbattery configuration.[2] However not much attention has been paid to understand the importance of selecting an appropriate lithium precursor for controlling the thin film properties and conformality, even though Li-TP materials are highly desirable from the battery application point of view. Given their potential application in 3D thin-film microbatteries, understanding both conformality and thin-film coverage (penetration depth) are also crucial. In this research, we investigated the impact of different lithium precursors on the Li-TP thin film properties, conformality and penetration depth (PD). The lithium precursors evaluated were: lithium tert-butoxide (LiO^tBu), lithium bis(trimethylsilyl)amide (Li-HMDS) and lithium 2,2,6,6-tetramethyl-3,5-heptanedionate (Li-THD); for the first two precursors the ALD/MLD process was developed/optimized as they had not been previously employed for the Li-TP thin film growth. For conformality measurements, we utilized lateral high-aspect-ratio (LHAR) PillarHall[3] structures and a novel imaging ellipsometry technique that enables film thickness determination even at Ångström level. To support the experimental work, a detailed computational survey of the precursors was conducted. Through DFT optimizations combined with highly accurate DLPNO-CCSD(T) energy calculations the most prevalent oligomeric forms under typical ALD conditions were determined; the effective diameter (d_{eff}) and mean free path (MFP, λ) of the precursor's oligomeric form were found to play a major role in determining the conformality characteristics of the resultant Li-TP thin films (Figure 1). Among the three precursors investigated, Li-HMDS was found to result in Li-TP thin films with superior conformality characteristics. The current approach of using theoretical calculations to predict film conformality based on precursor molecular structure can significantly reduce the amount of experimental work required and streamline the screening process for precursors aimed at enhancing conformal coating.

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Applied Surface Science
Room Ballroom A - Session AS-ThP
Applied Surface Science Poster Session

AS-ThP-1 Scratching at the Surface of Leadership, ***Brian Strohmeier,*** Surface Science Solutions, LLC

In today's dynamic research and business environment, strong technical skills are essential, but insufficient, for sustained career growth. Many exceptional scientists find themselves promoted to first-level management roles because of their outstanding scientific achievements, usually without having any formal training in leading people. Although they are well-prepared in technical and scientific areas, the toughest challenges for new managers usually involve delicate interpersonal skills, such as active listening, conflict resolution, empathy, and emotional intelligence, rather than science itself. Such topics are rarely encountered in graduate-level education and almost never in undergraduate curricula. To thrive amid constant change, managers and technical leaders need to hone and adapt their leadership styles to optimize resource management for each situation, focusing on prioritizing, empowering, and motivating their teams. This poster presentation will highlight effective modern leadership skills and strategies that can enhance your personal long-term growth and boost your career success.

AS-ThP-3 Sample Preparation Checklists and Instrument Parameter Tables: Newly Published Aids to Reliable and Reproducible Surface Analysis Data, Paper Reviewing, and Information Reporting, ***Don Baer,*** Pacific Northwest National Laboratory; *Linda Dake,* retired

Several examinations of surface analysis information reported in the literature indicate a significant degree of flawed data analysis and a high degree of inadequate reporting regarding sample handling, instrument operation and analysis details. This poster provides information about two newly published “tools” intended to help address three issues:

1. Researchers and others with surface analysis needs, but unfamiliar with the sample handling requirements often present “damaged” samples for analysis.
2. Information about how a sample has been handled before and in preparation for surface analysis is often not provided, and may not be recorded, limiting the ability of others, looking at a data report or in a publication, to assess the reliability of the analyses.
3. Many publications do not contain either adequate sample or instrument information to assess the data quality or to verify adequacy for use in databases or AI input

To assist those unfamiliar with collecting and preparing samples for surface analysis and to assist surface analysts in collecting data that should be recorded, two checklists based on new ISO standards have been published in the open literature. The first checklist is designed to guide a sample owner in selecting, handling and transporting a sample to a surface analyst. The second checklist is intended to assist a surface analyst in obtaining and reporting information regarding sample treatment, processing and mounting for surface analysis. These are based on ISO standards 20579 part 1: Documenting and reporting the handling of specimens prior to analysis and ISO 20579 part 2, Documenting and Reporting the Preparation and Mounting of Specimens for Analysis. In addition to the reporting requirements, which include information about the sample history and analysis objectives, there are normative annexes that provide information about sources of sample contamination, ways to minimize contamination and expected or generally required components of sample handling to extract useful surface information.

A new series of papers in Surface Science Spectra is being published to help analysts and authors report the relevant instrument information and provide readers with the information needed to assess the meaning and quality of XPS data. Included in these papers are instrument parameter tables which provide both the “fixed” instrument parameters and those that are operator selected and need to be called out in reports and journal articles.

The poster will show the checklists and examples from published parameter tables.

AS-ThP-4 Atmosphere-Controlled Surface Engineering of $CuRh_2O_4$ Nanofibers For Alkaline Water Oxidation, ***Namhee Kim,*** *Hyeon Gyeong Jeon, Myung Hwa Kim,* Ewha Womans University, Republic of Korea; *Dasol Jin,* Jeonbuk National University, Republic of Korea

Controlling the surface chemical states of metal oxide electrocatalysts is critical for optimizing catalytic performance, yet Cu-based oxides pose a particular challenge since Cu readily shifts its oxidation state depending on the synthesis atmosphere. In this work, Cu-Rh bimetallic oxide nanofibers were prepared by electrospinning followed by post-annealing under controlled O_2/He flow, where the O_2 concentration was systematically varied to examine its effect on surface composition and phase evolution. AR-XPS analysis revealed that insufficient oxidation leaves Cu and Rh incompletely oxidized, while excess oxygen promotes unwanted secondary phase formation. Only at the optimized O_2 concentration were Cu^{2+} and Rh^{3+} simultaneously stabilized on the surface, and single-phase $CuRh_2O_4$ formation was verified by XRD and Raman spectroscopy. The phase-pure sample demonstrated superior oxygen evolution reaction (OER) activity in 1 M NaOH, outperforming commercial Ir/C, along with stable performance over extended operation. These results highlight that annealing atmosphere engineering is a straightforward yet powerful route to controlling surface chemical states and achieving phase-pure Cu-based spinel oxide electrocatalysts. This work was supported by the National Research Foundation of Korea funded by the Ministry of Science and ICT and the Ministry of Education. (NRF-RS-2018-NR031064 and RS-2025-16063688).

AS-ThP-5 Surface Chemical Characteristics of Electrospun Multicomponent Rutile Oxide Nanofibers for pH-Universal Oxygen Evolution Reactions, ***HyeonGyeong Jeon,*** *Namhee Kim, Youngmi Lee, Myung Hwa Kim,* Ewha Womans University, Republic of Korea

Lattice-entropy modulation in multicomponent oxide systems has attracted increasing interest as a strategy for tuning surface chemical environments and interfacial electrocatalytic properties. In this study, rutile-type $(RuIrCrMnSn)O_2$ nanofibers were fabricated via electrospinning followed by thermal treatment. Electron microscopy and elemental mapping analyses confirmed the formation of continuous fibrous structures with relatively uniform distributions of Ru, Ir, Cr, Mn, and Sn species throughout the oxide framework. X-ray diffraction, SAED, and Raman analyses supported the formation of rutile-related multicomponent oxide structures with broadened structural features associated with multication incorporation. X-ray photoelectron spectroscopy revealed mixed oxidation states and defect-related oxygen species on the oxide surface, indicating chemically diverse surface environments within the multicomponent oxide structure. Among the prepared samples, the $(RuIrCrMnSn)O_2$ nanofibers calcined at 400 °C exhibited overpotentials of 199.7, 244.4, and 330.1 mV at 10 mA cm^{-2} under acidic, alkaline, and neutral electrolytes, respectively. The optimized sample also maintained stable operation for up to 35 h in acidic electrolyte. These results suggest that multicomponent rutile oxide nanofibers can provide chemically diverse electrocatalytic interfaces for pH-universal oxygen evolution reactions. This work was supported by the National Research Foundation of Korea funded by the Ministry of Science and ICT and the Ministry of Education. (NRF- RS-2025-16063688).

AS-ThP-6 Industrial Problem Solving with Low-Cost ToF-SIMS, *Nick Long, Torsten Henkel,* SAI, UK; ***Aidan Harrison***, *Silverio Iacono,* SAI Americas

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is often perceived as a complex high-end research tool requiring extreme mass resolution and accuracy. However, lower cost ToF-SIMS systems with restricted mass resolution operating at high vacuum levels for increased sample throughput remain exceptionally powerful for troubleshooting the processing of materials in industrial environments. These instruments can provide actionable data for resolving production bottlenecks, including (but not limited to) those arising in the following application areas.

Resolving Adhesion Failures

Adhesion problems in industrial processes often stem from monolayer-level surface modifications that are invisible to bulk analysis techniques. Low-cost ToF-SIMS excels here by identifying functional group distributions at the interface. For instance, the technique can detect sub monolayer presence of mold release agents (such as silicones or stearates) which can negatively impact adhesion performance. Additionally, a detailed inspection of the mass spectra from such surface contaminants can distinguish any subtle molecular differences between them in order to identify likely sources.

Detecting and Identifying Industrial Cleaning Residues

In a production electronics environment, contamination issues which can affect the performance of assembled parts often involve residues left by cleaning processes. These residues will have distinct signatures or fragmentation patterns that can be measured by ToF-SIMS even without high-resolution mass separation, helping to trace the source of the issue back to a specific stage in the manufacturing line such as a contaminated wash bath.

Detecting and Identifying Corrosion under Painted Metal Surfaces

Filiform corrosion is an atmospheric corrosion affecting organic coated metals by producing “threadlike” residues beneath the coating. Scanning Kelvin Probes can detect problems beneath the coatings physically by measuring work functions but for absolute chemical identification of the surface corrosion products a Low-Cost ToF-SIMS can provide the necessary answers.

Optimizing LDPE Roll Packaging Efficiency

The efficiency of Low-Density Polyethylene (LDPE) roll packaging often depends on the controlled migration of additives, specifically slip agents such as erucamide. These additives must bloom to the surface in precise concentrations to reduce friction during high-speed packaging processes. Restricted mass resolution ToF-SIMS is highly effective at monitoring the surface coverage of these slip agents, helping to resolve any blocking issues in the packaging process.

AS-ThP-7 Analysis of Interfaces by Soft and Hard X-ray Photoemission, ***Jia Lu***, *Jennifer Mann, Sarah Zaccarine, Norb Biderman, Cesar Saucedo, Kateryna Artyushkova,* Physical Electronics USA

Recent developments of lab-based hard X-ray photoelectron spectrometers (HAXPES) have created new, accessible opportunities for routine analysis of technologically significant devices. A micro-focused, monochromatic Cr Kα X-ray source not only provides three times greater analysis depth in comparison to the traditional Al Kα X-ray source, but it also provides high sensitivity for small area analysis. Using a combination of soft and hard X-rays allows for the analysis of materials non-destructively for their in-depth compositional heterogeneities. For film thicknesses that require ion beam sputtering to reach buried interfaces and layers, Cr sources allow one to probe below the depth of ion beam damage.

This poster will showcase how combining soft and hard x-ray photoemission within a single laboratory instrument offers a robust, non-destructive solution for chemical state analysis across the surface to bulk depth range. By using the micro-focused, monochromatic Cr X-ray source with increased analysis depth, accurate bonding chemistry and stoichiometry ratio of Ti/Al flakes (less than 100µm in diameter) can be probed below the surface organic contaminations with high sensitivity. In combination with soft X-rays, hard X-rays provide improved insight of how the NiPt nanowire surface was affected by annealing and surface treatments. Using a combination of XPS and HAXPES, high accuracy was obtained for calculating the thin film layer thickness of carbon/HfO_2/SiO_2/Si substrate using *Strata*PHI. For depth profile analysis of tin oxide, Cr X-ray source shows lower degree of tin reduction in comparison to Al X-ray source, showcasing its capability to probe below the depth of ion beam damage.

AS-ThP-8 Ion Scattering Spectroscopy to Identify and Quantify Selective Internal and External Decorations of Pt Nanoparticles on Porous Carbon Supports, ***Alessio Cosenza***, *Ich Tran, Plamen Atanassov,* University of California Irvine

Determining whether metal nanoparticles are located on the external surface or within the internal pore network of porous supports remains a key challenge in applied surface analysis, catalyst design, and host–guest nanomaterials. This distinction is especially important for porous carbon-supported Pt catalysts, where nanoparticle locality affects accessibility, utilization, and stability. However, common characterization methods provide incomplete information. TEM and dark-field imaging give projected contrast through the specimen thickness, making internal and external nanoparticles difficult to distinguish. Secondary-electron imaging is more surface-sensitive, but remains qualitative and can be ambiguous for nanoparticles beneath nanometer-scale carbon shells. XPS provides surface and chemical sensitivity, but Pt beneath thin carbon shells can still contribute to the Pt 4f signal because of the finite information depth.

Here, we investigate ion scattering spectroscopy (ISS) as a direct surface-sensitive approach to distinguish externally exposed Pt nanoparticles from Pt shielded inside mesoporous carbon black supports. Pt nanoparticles with similar size distributions were synthesized either within the carbon shell/pore network or on the external carbon surface. Carbon supports with different shell thicknesses and graphitic structures were used to evaluate how nanoparticle confinement affects the ISS and XPS response.

For each matched internal/external Pt pair, the external-Pt catalyst was used as a local reference corresponding to fully externally accessible Pt. The Pt ISS signal of the internal-Pt catalyst was normalized by total Pt loading and compared with the corresponding external reference. This provides a semi-quantitative estimate of the fraction of Pt accessible to the outermost surface. The complementary XPS response was used to evaluate how much of the internal Pt population remains detectable through the carbon shell, providing an apparent Pt 4f visibility factor rather than a direct measure of external exposure.

The results show that ISS can resolve large differences in external Pt accessibility between nominally similar Pt/C catalysts and estimate the fraction of nanoparticles shielded within the pore/shell structure. In contrast, XPS and electron microscopy provide valuable complementary information but cannot alone quantify nanoparticle locality in these non-ideal porous systems. This work establishes ISS as a practical surface-analysis tool for evaluating nanoparticle placement in porous catalyst supports and suggests broader application to host–guest, core–shell, encapsulated catalyst, and carbon peapod-type nanostructures.

AS-ThP-9 Probing Energy Level Alignments in NFA Organic Solar Cells: Combined UPS and LEIPS Study on Blend Films, ***Yongsup Park***, *Seunggu Lee,* Kyung Hee University, Republic of Korea

Energy level alignment (ELA) in non-fullerene acceptor (NFA) organic photovoltaic (OPV) cells is crucial, as the offsets between HOMO and LUMO levels at the bulk heterojunction (BHJ) interface determine charge separation efficiency and significantly affect the open-circuit voltage (Voc). Traditionally, ELA has been measured using a combination of cyclic voltammetry (CV) and optical absorption (OA), despite their limited accuracy. More precise measurements can be obtained through UV photoemission spectroscopy (UPS) and low-energy inverse photoemission spectroscopy (LEIPS). However, most studies have focused on neat films, while ELA can differ significantly in blend films. In this study, we used UPS and LEIPS to measure the HOMO and LUMO levels for both neat and blend films of the donor-acceptor pairs (PM6:Y6 and PM6:L8-BO). The results reveal significantly different ELA in blend films compared to neat films, particularly when using conventional vacuum level alignment was applied to the neat films. These differences are discussed in the context of Voc estimation and the impact of the HOMO offset (ΔE_HOMO) on charge separation efficiency.

AS-ThP-10 Tuning Topography and Morphology of Mg2-MOF-74 Metal-Organic-Framework to Study Optimization of Carbon Capture Capabilities, ***Corbyn Stosich***, *Sean Lubner,* Boston University

In order to combat the climate crisis and keep global warming under the 1.5℃ threshold for human safety, it is imperative that our net carbon emissions reach not only zero, but be negative by 2050 [1], [2]. To accomplish negative emissions, carbon capture via direct air capture (DAC) and point capture are necessary and on the scale of gigatons per year [3]. This process is energetically exhaustive due to the thermal energy required to regenerate carbon capture materials, and these energy demands cannot be met by global energy production [2], [3].

Metal organic frameworks (MOFs) are a highly tunable class of materials that have demonstrated exciting abilities in adsorption of CO_2 for point capture and primarily DAC purposes. These materials have particularly high CO_2 capacity with incredibly fast kinetics. The tunable nanostructure inherent to MOFs allows for many ways to minimize the energy requirement of material regeneration.

In this work, we tweak synthesis environments of otherwise identical MOF materials (Mg_2-MOF-74) to study the resulting topography and morphology. This process is accomplished through heterogeneous crystallization on different substrates with varying temperature and polarity environments. We then characterize the resulting crystals by running BET, SEM, and NMR to identify both surface and chemical variances. We aim to isolate variables such as crystal length and orientation, porosity, pore percent, and surface area. These factors influence the MOF’s ability to capture CO_2 as capacity, kinetics, and selectivity are affected and measured by TGA and our house dynamic gas sorption system. By tuning the nanostructure of these materials, we aim to optimize these variables to alleviate the energy burden of sorbent regeneration.

References:

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AS-ThP-11 XPS Analysis of Plasma Exposed TiB2 and ZrB2 Substrates, ***Harry Meyer***, *Lauren Nuckols, Chad Parrish,* Oak Ridge National Laboratory

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

AS-ThP-12 Thin-Film Characterization Using the Surface Analysis Toolbox: From Data to Answers, ***Jonathan Counsell***, Kratos Analytical Limited, UK

Thin films play a critical role in semiconductor devices and coatings due to their unique physical and chemical properties. Accurate characterization of these films is essential for understanding their behaviour and optimizing their performance. The surface analysis toolbox, including techniques such XPS, HAXPES and both destructive and non-destructive methods.

In this study, we utilize the surface analysis toolbox to characterize metal oxide and nitride thin films focusing on the interfacial regions where different materials meet. We employ XPS to determine the chemical states of elements in the thin films, particularly focusing on interfacial oxidation states. HAXPES is used to complement XPS by providing information on the elemental composition and depth profiling of the thin films.

By integrating these surface analysis tools, we capture detailed information about the chemical interactions and electronic configurations at the interfaces. Our work aims to bridge the gap between raw data and meaningful interpretations, providing a comprehensive understanding of the thin-film characteristics. Through optimized sample preparation and advanced data analysis techniques, we offer insights into the fundamental properties of thin films, enabling the development of more reliable and efficient semiconductor technologies.

AS-ThP-13 Cryo-XPS of nanoparticles. Vitrification... where speed is everything!, ***Chris Moffitt***, Kratos Analytical Inc.*; Liam Soomary,* kratos Analytical Inc, UK

Vitrification, a rapid cooling process that prevents ice formation, is crucial for preserving the structural integrity of nanoparticles during cryogenic applications. In this study, we employ Cryo-XPS (X-ray Photoelectron Spectroscopy) to investigate the surface chemistry and phase transformations of various nanoparticle types during the vitrification process. Our findings highlight the importance of ultrafast cooling rates in maintaining the desired physical and chemical properties of these materials. We discuss the challenges associated with achieving uniform vitrification across different nanoparticle sizes and compositions and propose strategies to optimize and improve experimental workflows during the vitrification process for enhanced material stability and performance. These insights are particularly relevant for applications in nanotechnology, biomedicine, and advanced materials science.

AS-ThP-14 Surface and Bulk Characterization of Organic Macrocyclic Coordination Compounds Using XPS and UPS Techniques, ***David Surman***, Kratos Analytical Inc.

Organic semiconductors have gained attention due to their potential for flexible, lightweight, and low-cost electronic applications. These materials enable charge transport via delocalized electronic states, a characteristic of their pi-conjugated molecular structures. Their utility includes various organic electronic devices, such as Organic Thin-Film Transistors (OTFTs) and Organic Photovoltaics (OPVs). The selection and performance of these materials depend on properties such as charge carrier mobility, energy level alignment, and stability. Here we utilize a combination of experimental methods - XPS and XPS imaging, to probe the surface and bulk properties of both blanket and printed organic semiconductor structures. We will discuss the relevance of scattered electron backgrounds and background subtraction for analytical clues. Also, we will explore the effects of deposition processes and the evolution of electrical properties as a function of depth using Argon cluster etching ultra thin layers. UPS is also used in with profiling to give not just an elemental distribution but also the electronic properties of these molecules as a function of depth, determining the work function of these materials, a critical parameter in optimizing charge injection and transport. A methodological approach to surface characterization will also be discussed, providing insights into the interfacial properties that govern device performance.

AS-ThP-15 Automatically Determining the Cutoff of the Transfer Function in Reciprocal Space for the Fourier Denoising of X-ray Photoelectron Spectroscopy Data, ***Tyler B. Andersen***, *Maxsym Gerashchenko, David E. Aspnes, Matthew R. Linford,* Brigham Young University

The Fourier denoising of X–ray photoelectron spectroscopy (XPS) data is valuable when optimal (low noise) XPS data cannot be collected. It should also prove to be important when preparing XPS data for analysis by artificial intelligence (AI). Because of its sigmoidal shape in reciprocal space, its adjustable position, and the shape of its Fourier transform in real space, the Gauss-Hermite transfer function is an excellent transfer function for denoising data. However, the position of this transfer function on a set of Fourier coefficients is determined manually by the user. In this work, we describe two algorithms for automating this positioning. It is believed that these algorithms will also work for other transfer functions, e.g, the brick wall filter function. In addition, these approaches should apply well to data from other techniques, for example, spectroscopic ellipsometry, low-energy electron scattering, and x-ray diffraction, among others.

AS-ThP-17 Heterointerface-Induced Charge Transfer Kinetics in Sputtered $Mote_2$-Mos_2 Nanocomposite for High-Performance Ambient No_2 Detection, *Sonika Kodan,* ***Ramesh Chandra***, Indian Institute of Technology Roorkee, India

The present research reports a nanostructured $MoTe_2$-MoS_2 n-n heterojunction-based gas sensor developed on a silicon (Si) substrate, demonstrating room-temperature (RT, 30 °C) nitrogen dioxide (NO_2) sensing. A controlled and one-step magnetron co-sputtering approach is utilized to deposit $MoTe_2$-MoS_2 nanocomposite thin film on a Si substrate, producing a uniform, dense, and porous nanoscale morphology. Herein, surface analysis and structural characterization of the $MoTe_2$-MoS_2/Si sensor reveal a rough, and defect-rich morphology with abundant exposed edge sites, which significantly enhances the availability of active adsorption sites for effective gas sensing. The developed $MoTe_2$-MoS_2/Si heterostructured sensor delivers an exceptional sensor response of 74.4% with an ultrafast response/recovery time of 7.5/2 s towards 25 ppm NO_2 at RT. Additionally, the present sensor showcases highly reproducible and consistent behavior over a wide range of NO_2 concentrations (1-60 ppm), along with remarkable selectivity against common potential interfering gases (H_2S, NH_3, CO, H_2) and a low detection limit of 700 ppb. This study provides critical insights into NO_2 sensing induced by heterointerface band modulation and defect-assisted adsorption at the sensor's surface, thereby providing a strong foundation for a reliable platform for high-performance NO_2 gas sensors based on the MoTe2-MoS2 heterostructure.

AS-ThP-18 ASSD Student Award Finalist Poster: Sen-Banerjee (SB) Number as a Unified Scaling Parameter for Deviant Density Enhancement in Nanofluids, ***Anusree Sen***, *Debjyoti Banerjee,* Texas A&M University

Nanofluids are attractive for modulating heat transfer (thermal management), energy storage (e.g., battery), transport, and radiation-shielding applications because adding nanoparticles can anomalously change the effective properties of a base fluid (neat solvent). In practice, measured property changes (e.g., density) do not match the classical two-

phase mixture model predictions. This mismatch is usually tied to interfacial effects near the particle surface that standard models do not include.

In this study, we evaluate the Sen-Banerjee number (S_B) as a practical scaling parameter for interpreting and predicting these anomalous density deviations. The analysis leverages a three-phase model of a nanofluid: the nanoparticle, the surrounding bulk liquid, and a compressed interfacial liquid layer formed at the solid-liquid boundary (this is also termed as the "*nano-Fin effect*" or "*nFE*"). We tested the framework across three representative nanofluid families, molten-salt nanofluids, poly-alpha-olefin nanofluids, and casein oleo-nanofluids, while varying nanoparticle shape, nanoparticle mass fraction, and interfacial-layer thickness.

A clear pattern emerges when surplus density is plotted against the Sen-Banerjee number (S_B). Interestingly, results from different systems and particle geometries collapse toward a common trend. At low S_B, density enhancement is stronger and highly sensitive to small changes in concentration. At higher S_B, the response gradually approaches classical mixture-rule behavior (two-phase mixture rule). Among the systems studied, casein oleo-nanofluids show the strongest deviations, consistent with their density contrast between phases. Overall, SB offers a physically meaningful and scalable way to compare nanofluids and guide formulation choices for targeted applications.

KEYWORDS: Sen-Banerjee number; nanofluids; deviant density; interfacial compressed layer; nano-Fin effect; thermophysical properties; scaling analysis; density enhancement, anomalous property, nFE.

AS-ThP-20 A Priori designed NiAg Single-Atom Alloys for Selective Epoxidation Reactions, ***E. Charles H. Sykes,*** Tufts University

Ethylene oxide, produced through the partial oxidation of ethylene, is one of the highest-volume chemicals manufactured globally—and also one of the most carbon-intensive. While silver (Ag) catalysts can achieve high selectivity (~90%) for ethylene oxide, this requires a combination of promoters such as chlorine (Cl), which increases selectivity by 25%, cesium (Cs), and rhenium (Re). The reaction must also be run at low conversions (<15%) to prevent complete combustion of ethylene to CO_2. In this work, we present a theory-guided investigation showing that the incorporation of small amounts of nickel (Ni) into Ag(111) surfaces lowers the activation barrier for O_2 dissociation and facilitates the spillover of atomic oxygen onto the Ag surface. Temperature-programmed desorption (TPD) experiments confirm the facile dissociation, spillover, and desorption of O_2 on NiAg(111). Remarkably, and in contrast to previous studies, Ni enables the formation of atomic oxygen on Ag(111) under near-ultra-high vacuum conditions without the need for oxygen atomizers or reactive species like NO_2 or O_3. Ambient pressure X-ray photoelectron spectroscopy (AP-XPS) further reveals that Ni not only promotes O_2 activation and spillover but also stabilizes nucleophilic oxygen species, which are typically associated with total combustion pathways. Guided by these findings, we synthesized and tested supported catalysts, demonstrating that NiAg single-atom alloy nanoparticles improve both conversion and ethylene oxide selectivity by 25%—achieved without the use of Cl, the ubiquitous industrial promoter.

Reference

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Advances in Battery Engineering, Interface Design, and Characterization Mini-Symposium
Room Ballroom A - Session BT+AS+CA+TF-ThP

Advances in Battery Engineering, Interface Design, and Characterization Mini-Symposium Poster Session

BT+AS+CA+TF-ThP-1 Orientated Deposition of Li2S for Fast-Charging Lithium-Sulfur Batteries, *Jeong-Hoon Yu,* ***Jong-Sung Yu,*** DGIST, Republic of Korea

Precipitation/dissolution of insulating Li_2S has long been recognized as the rate-determining step in lithium–sulfur (Li–S) batteries, which dramatically undermines sulfur utilization at elevated charging rates. Herein, we present an orientated Li_2S deposition strategy to achieve extreme fast charging (XFC, ≤15 min) through synergistic control of porosity, electronic conductivity, and anchoring sites of electrode substrate. Via magnesiothermic reduction of a zeolitic imidazolate framework (ZIF), a nitrogen-doped and hierarchical porous carbon with highly graphitic phase was developed. This design effectively reduces interfacial resistance and ensures efficient sequestration of polysulfides during deposition, leading to (110)-preferred growth of Li_2S nanocrystalline between (002)-dominated graphitic layers. Our approach directs an alternative Li_2S deposition pathway to the commonly reported lateral growth and 3D thickening growth mode, ameliorating the electrode passivation. Therefore, a Li–S cell capable of charging/discharging at 5C (12 min) while maintaining excellent cycling stability (82% capacity retention) for 1000 cycles is demonstrated. Even under high S loading (8.3 mg cm^{-2}) and low electrolyte/sulfur ratio (3.8 μL mg^{-1}), the sulfur cathode still delivers a high areal capacity of >7 mAh cm^{-2} for 80 cycles.

BT+AS+CA+TF-ThP-2 High Voltage Li-ion Battery Cathodes: Surface Fluorination and Transition Metal Doping of Lithium Cobalt Oxide (LCO), ***Falak Sher,*** *Carlos Yescas, Timothy Spila, Arghya Patra, Ben Zahiri, Paul Braun,* University of Illinois at Urbana-Champaign, USA

Lithium cobalt oxide cathode (LCO) is extensively used as a cathode material in lithium-ion batteries for portable electronics. It is among the highest-performing cathode materials because of its structural stability, long cycle life, and high volumetric density at a cut-off voltage of 4.2 V (vs. Li/Li^+). Significant energy density increases would be provided by lifting the cut-off voltage from 4.2 V to 4.6 V (vs. Li/Li^+), increasing the specific capacity from 140 mhA/g to 200 mAh/g. However, at high-voltages, the cathode material undergoes severe challenges such as unstable cathode-electrolyte interface (CEI), undesirable permanent phase transformations, and oxygen loss which limit energy density and cycle life. To improve the high-voltage stability and electrochemical performance of LCO, we demonstrate plasma-assisted surface modification and fluorine, and transition metal doping. Incorporation of fluorine, in combination with transition elemental doping, protects the surface by reconstructing the layered structure of LCO into a short-range disordered rocksalt structure. Once protected, the LCO can be cycled to higher voltages, resulting in enhanced energy density and cycle-life. Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) analysis of both untreated and plasma engineered LCO confirms fluorination of the surface of plasma treated LCO. X-ray Fluorescence (XRF) and ToF-SIMS analyses of the plasma modified and pristine LCO show the incorporation of transition metals in the surface. High resolution STEM indicates that the surface is reconstructed from a layered LCO structure to a local disordered rocksalt structure. SEM images of the pristine and plasma treated LCO before and after cycling clearly show the increased stability of the plasma-treated material. surface modifications. At higher cycling voltages (4.6 V vs Li/Li^+) plasma modified LCO cathodes show significantly improved electrochemical results including longer cycle life, higher capacity retention, and higher energy density.

BT+AS+CA+TF-ThP-3 Development and Characterization of Sputtered Thin-Film Solid Electrolyte for Microbattery Applications, ***Ananya Bansal,*** *Ramesh Chandra,* Indian Institute of Technology Roorkee, India

Thin-film solid electrolytes are gaining significant attention for next-generation microbatteries due to their high safety, compact size, and compatibility lab on chip electronic devices. In this work, thin-film solid electrolyte was fabricated using RF magnetron sputtering, a scalable technique that enables precise control over film thickness, composition, and uniformity. The deposited films were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS) to investigate their structural, surface, and chemical properties. Electrochemical impedance spectroscopy (EIS) was employed to evaluate the ionic conductivity, activation energy, and interfacial behavior of the thin films. The influence of sputtering parameters on the microstructure and electrochemical performance of the electrolyte films is discussed. The results demonstrate that sputtered thin-film solid electrolytes exhibit good film uniformity, dense morphology, and high ionic transport conductivity (~10^3 S/cm) suitable for microbattery integration. This study highlights the potential of sputtering-based thin-film electrolytes for the development of compact, reliable, and high-performance all-solid-state microbatteries for wearable electronics, IoT devices, and miniaturized energy storage systems.

BT+AS+CA+TF-ThP-4 Fabrication and Characterization of the Thin Film Solid State Li and Na Ion Batteries, ***SATILMIS BUDAK,*** *Zhigang Xiao, Mebougna Drabo, Aschalew Kassu, Richard Lagle, Jamar Dozier, Kendall Montgomery, Kelvin Perkins,* Alabama A&M University

In this project, thin films of $LiCoO_2$ (cathode), LiPON (solid electrolyte), Sn (anode), and a multilayer stack combining these materials were deposited on silicon and silicondioxide substrates using electron-beam evaporation.

Samples were annealed at 50°C, 100°C, and 150°C, with unannealed films serving as a baseline. Electrical properties were observed using a Van der Pauw measurement system to obtain resistivity, mobility, carrier density, Hall coefficient, and sheet resistance, and were complemented by current–voltage (I–V) characterization for each material and for the multilayer stack. Further analysis involved Seebeck analysis and Scanning Electron Microscopy/Energy-Dispersive X-ray Spectroscopy (SEM/EDS) to observe sample thermoelectric properties and microstructure. Similar studies are being under study for Na ion batteries. Finding will be shared during the meeting.

Advances in Battery Engineering, Interface Design, and Characterization Mini-Symposium
Room 319 - Session BT+AS+CA+TF-FrM

Solid-State Batteries

Moderators: Prof. Alexander Kozen, University of Vermont, **Prof. Chuan-Fu Lin**, Catholic University of America

8:15am **BT+AS+CA+TF-FrM-1 Grain Structure Control of Evaporated Li Metal Films for Optimized Solid State Batteries**, ***Andrew Westover***, *Peyton Carden,* Oak Ridge National Laboratory, USA **INVITED**

Lithium metal is a critical anode material for next-generation, high-energy batteries. To realize these batteries, the lithium metal must be between thick, depending on the cathode chemistry. Furthermore, lithium metal must have controlled surface chemistry and high purity for optimal performance. Thermal evaporation is one of the most effective methods for producing thin lithium metal films that meet these criteria. In this work, we present our efforts to understand how to produce lithium metal films as thin as , and we explore the ability to fabricate lithium metal thin films with controlled microstructures. We have developed a process to modify the as-deposited lithium metal grain size in evaporated films from . Using these thin films with standard liquid electrolytes, localized high-concentration electrolytes, and solid electrolytes lead to significant differences in the cycling performance of lithium metal films. This work demonstrates the critical importance of microstructure control for realizing next-generation, high-energy lithium metal batteries.

This work was funded by the United States Department of Energy Transportation Technology Office Battery Materials Research Program and German-US Collaboration on Energy Storage under Simon Thompson and Tien Duong.

8:45am **BT+AS+CA+TF-FrM-3 Unravelling the Mechanism of Al2O3 Atomic Layer Deposition on Li_6PS_5Cl for All-Solid-State Batteries**, *Kyobin Park, Donghyeon Kang, Taewoo Kim, Vepa Rozyyev, Anil Mane, Hacksung Kim, Francisco Vargas, Zachary Hood, Peter Zapol, Justin Connell,* ***Jeffrey Elam***, Argonne National Laboratory

Sulfide superionic conductors with the argyrodite structure (e.g., Li_6PS_5Cl, LPSCl) are extremely promising for all solid-state batteries, but poor atmospheric stability and high interfacial reactivity limit their widespread adoption. Coating LPSCl powders with ultrathin, metal oxide coatings using atomic layer deposition (ALD) mitigates these problems, protecting LPSCl against atmospheric degradation[1] and reducing reactivity with Li metal, yielding more stable cycling[2]. Despite significant promise, the ALD mechanism is unknown, hampering the development of new coating chemistries.

In this study, we elucidate the mechanism for Al_2O_3 ALD on LPSCl using trimethyl aluminum (TMA) and H_2O by combining *in situ* Fourier transform infrared spectroscopy measurements and *ex situ* solid-state magic angle spinning nuclear magnetic resonance, UV Raman spectroscopy, and X-ray photoelectron spectroscopy measurements with density functional theory calculations. We determine that ALD Al_2O_3 nucleates promptly via TMA reaction with native -OH, -SH, and PS_3-OH groups to form transient C-Al-O(S) species that are rapidly hydrolyzed during the subsequent H_2O exposure. This reversible transformation maintains surface nucleophilicity and prevents sulfide decomposition. The resulting layer-by-layer growth leads to highly conformal Al_2O_3 coatings on LPSCl.

This detailed understanding of ALD surface reactions provides critical insights guiding the selection of future ALD chemistries with greater enhancement in cycling performance.

1. *Acs Materials Letters* **2024,** 6, (12), 5409-5417.
1. *Advanced Materials* **2023,** 35, (21), 13.

9:00am **BT+AS+CA+TF-FrM-4 Engineered Cathode Chemomechanics Enables Ultra-Low Stack Pressure Solid-State Batteries**, ***Paul Braun***, University of Illinois Urbana-Champaign

In solid-state batteries, stresses resulting from electrode material chemomechanics are strongly coupled to solid electrolyte-electrode interface failures. Such failures are significant barriers to realization of practical Li metal solid-state batteries. While high external pressures can reduce these failures, the required pressures are impractical, and thus a different approach to reducing interface failures is required. We show that control of cathode chemomechanical stress provides an important path for realization of solid-state batteries which operate at commercially relevant low (e.g., <1 MPa) stack pressures. Using a series of cathodes with different chemomechanics we provide experimental evidence of the role of electrode chemomechanics in solid-state battery failure. Our model systems reveal that electrode chemomechanics significantly alter Li metal plating and stripping behavior at low stack pressure. We utilize these learnings to build long cycle-life solid-state batteries with practical areal capacity (5 mAh/cm^2) operating under a 1 MPa stack pressure and at room temperature. Our findings highlight the importance of controlling positive electrode chemomechanics to realize low stack pressure solid-state batteries.

9:15am **BT+AS+CA+TF-FrM-5 Pulsed Laser Deposition of Solid Electrolytes: How Limited Thermal-Budget Processing Relates to Li-ion Conductivity**, *Nicola Perry,* University of Illinois*; En Ju Cho, Kai-Wei Lan,* ***Nicola Perry***, University of Illinois Urbana-Champaign **INVITED**

Near-room-temperature, thin-film deposition of air-sensitive Li-ion conductors can enable multilayer solid electrolytes and coatings for high-energy-density batteries and microdevices, compatible with thermally sensitive components. We investigate the capabilities of pulsed laser deposition for fabrication of high-quality layers of low-voltage- and high-voltage-stable solid-electrolyte compositions, including low-melting antiperovskite hydroxyhalides and higher-melting nasicon-structured oxides that contain glass-forming elements. The influence of growth parameters such as temperature, pressure, and laser fluence on stoichiometry, density, roughness, crystallinity, and conductivity is explored. Grazing-incidence nuclear reaction analysis paired with Rutherford backscattering spectrometry provides insight into light-element stoichiometry (e.g. Li, Cl, P) and the expected loss of Li (e.g.) with increasing temperature (given its volatility) and growth pressure (given its mass that enables scattering). Strategies to control stoichiometry of multiple light elements and deposition rates, through composite targets and sequential multi-target deposition, are demonstrated. X-ray reflectometry, grazing-incidence diffraction, and ellipsometry shape the understanding of structural dependence on growth parameters. We also examine the benefit of integrated impedance spectroscopy in the PLD chamber during and after growth to provide insights into transport behavior in a clean (air-free) environment as a function of temperature. We find most compositions benefit from vacuum deposition, but while the antiperovskite hydroxyhalides form single-phase, highly conductive films at room temperature, with phase decomposition and conductivity degradation above ~60 C, the nasicon-structured electrolytes benefit from post-deposition anneals to improve crystallinity and conductivity.

9:45am **BT+AS+CA+TF-FrM-7 Open-Circuit Energy Band Alignment at NMC/LLZTO and LLZTO/Li Interfaces for Solid-State Microbattery Applications**, ***Austine Amisi***, *Raquel-Garza Hernandez, Fabian Ambriz-Vargas,* Centro de Investigaciones en Óptica, Mexico

Stable electrode/electrolyte interfaces are critical for the electrochemical performance and long-term reliability of solid-state microbatteries. This work reconstructs the open-circuit energy band diagram of an all-solid-state $LiNi_xMn_yCo_zO_2$ (NMC)/$Li_7La_3Zr_{2-x}Ta_xO_{12}$ (LLZTO)/Li microbattery stack through band alignment analysis of the NMC/LLZTO cathode–electrolyte and LLZTO/Li electrolyte–anode heterojunctions. Thin-film bilayers were fabricated by RF magnetron sputtering and thermal evaporation. Valence and conduction band offsets (VBOs and CBOs) were experimentally determined using the Kraut method through conventional and angle-resolved X-ray photoelectron spectroscopy (XPS/ARXPS). A VBO of +3.13 ± 0.1 eV and a CBO of −6.00 ± 0.1 eV were measured at the NMC/LLZTO interface, with a large CBO that suggests the formation of an electronically insulating interface that suppresses electrolyte decomposition at the cathode during charging. In contrast, a VBO of +1.92 ± 0.1 eV and a near-zero CBO of +0.08 ± 0.1 eV were determined at the LLZTO/Li heterojunction, indicating an electronically conductive interface that promotes electron accumulation and facilitates LLZTO degradation upon contact with the anode. An electrochemical potential window of 6.00 ± 0.1 eV and an open-circuit voltage of 3.29 ± 0.1 eV were obtained from the reconstructed full-stack band diagram. These results establish a direct link between interfacial band alignment and potential degradation mechanisms and provide critical design guidelines for advancing the operational stability of LLZTO-based solid-state microbatteries.

10:00am **BT+AS+CA+TF-FrM-8 LiPON-Enabled Reduction of V2O5 during Fabrication of Thin-Film Ionic Devices***, **Leopoldo Tapia-Aracayo**, David Stewart, Gary Rubloff,* University of Maryland College Park

Vanadium (V) Oxide (V_2O_5) is a well-researched layered oxide with high capacity (375 mAh/g), often cited for its applications in energy storage, electrochromic, and neuromorphic applications. In the field of thin-film ionic devices, we can sputter Lithium Phosphorus Oxynitride (LiPON) on top of crystalline V_2O_5, creating our electrolyte/electrode stack. This sequence simplifies the fabrication of thin-film ionic batteries as sputtering LiPON can insert Lithium up to 2 Li^+ per V_2O_5. We wanted to address the roughness of the LiPON/V_2O_5 interface by altering the fabrication steps to form a smooth interface, but unintentionally reduced the V_2O_5 to a VO_2 phase.

This smooth interface was achieved by sputtering amorphous V_2O_5 thin films in Ar/O_2 environment, then coated with LiPON, and subjected to post-deposition annealing in N_2 gas environment at 300 ◦C. The N_2 gas environment for the post-deposition annealing would crystallize the V_2O_5 and preserve the LiPON composition. We tracked the formation of a VO_2 phase, which was not observed for N_2 annealed V_2O_5 without LiPON, which remains VO_2 free. We used electrochemical cycling to probe the presence and evolution of the VO_2 phase, illustrating VO_2 reaction peaks instead of characteristic crystalline V_2O_5 peaks in the 2.2 V – 4.0 V vs Li+/Li window. (Seen in Figure 1). We will discuss how this behavior may be caused by LiPON-enabled reduction pathways at the buried interface. We confirm this reduction is limited to the interface as analysis via Raman identifies lithiated V_2O_5 phases. Systematic variation of LiPON sputtering parameters and annealing conditions, while holding LiPON thickness constant, reveal processing regimes that drive VO_2 formation versus preserving V_2O_{-5}. Ultimately, preserving the morphological benefits of a smooth LiPON/ V_2O_5 interface while constraining VO_2 formation, providing guidance for designing desired application-specific vanadium-oxide phases.

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