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)

Author Index

Bold page numbers indicate presenter