Thursday Evening, November 9, 2023

Applied Surface Science Division
Room Oregon Ballroom 203-204 - Session AS-ThP
Applied Surface Science Poster Session

AS-ThP-1 Low-Energy Ion Scattering Intensities from Supported Nanoparticles: The Spherical Cap Model to Determine Number Density, Size, and Contact Angle, ***Kun Zhao***, University of Washington; *D. Auerbach,* Max Planck Institute for Multidisciplinary Science, Germany; *C. Campbell,* University of Washington

Supported nanoparticles are of great importance to many technologies such as fuel processing, and catalyzed chemical synthesis, energy storage and generation, thin film fabrication, etc. Low energy ion scattering spectroscopy (LEIS) with noble gas ions like He^+ is a powerful tool for the characterization of nanoparticles dispersed across flat support surfaces due to its ability to probe the elemental composition in the topmost atomic layer of a surface, providing quantitative information regarding the size and number density of nanoparticles.Here, we present a derivation of the LEIS intensities expected from nanoparticles and the support material as a function of the average particle size, their number per unit area and their contact angle with the support when modeled as spherical caps of the nanoparticle material dispersed over the surface of a support. The model assumes that the ion intensities are determined only by the physical blocking of linear ion trajectories, and independent of the tilt angle of the local surface relative to the incident and scattered ion directions, an assumption we support by quantitative modelling of published data which tested tilt-angle effects. The model is a generalization to arbitrary contact angles of the hemispherical cap model which assumes 90˚contact angle and has been widely used to model spectroscopic signals from nanoparticle arrays in LEIS (and also in Auger and photoelectron spectroscopies). This new model quantitatively reveals how LEIS signals are sensitive not only to the diameter and number density of the nanoparticle, but also to their contact angle (or height : diameter ratio). With the use of additional data (e.g., from microscopies or adsorption microcalorimetry), the model presented here will enable more accurate determination of the average size, shape and number density of supported nanoparticles based on LEIS intensity measurements.

AS-ThP-2 Work Function Measurement by Ultraviolet Photoelectron Spectroscopy: Versailles Project on Advanced Materials and Standards Interlaboratory Comparison, ***Jeong Won Kim***, *A. Kim, H. Hwang, J. Kim, S. Choi,* KRISS, Republic of Korea; *N. Koch, D. Shin,* Humboldt University Berlin, Germany; *Z. Zhao, F. Liu,* CAS, China; *M. Choi,* SK Hynix, Korea; *K. Lee, Y. Park,* Kyung Hee University, Republic of Korea

Since the introduction of the work function (WF) through Einstein's photoelectric effect, it has become an important parameter for characterizing material surfaces. The WF governs charge injection/collection efficiency and charge transfer at material interfaces, making WF control and measurement crucial in many electronic and optical devices. Ultraviolet photoelectron spectroscopy (UPS) has been the primary method for measuring WF over several decades. However, reported WF values strongly depend on surface treatment and measurement conditions, even for the same material. Thus, it is necessary to develop a well-prepared guide to report reliable WF values.

To address this issue, we devised an interlaboratory comparison for WF measurement by UPS and present the results of a study conducted conducted under the Versailles Project on Advanced Materials and Standards (VAMAS). Two samples, a gold film deposited on a flat Si wafer and highly oriented pyrolytic graphite (HOPG), were distributed to six international laboratories. Prior to the UPS measurements, the samples underwent common treatment processes, including instrumental settings for energy-scale calibration and bias optimization. The Au sample exhibited a WF of 5.40±0.12 eV after Ar+ sputtering in vacuum, while the HOPG sample showed a WF of 4.61±0.09 eV after mechanical peeling-off. The narrow deviation in data among the laboratories for both high and low WF values will provide a basis for establishing a new international standard for UPS in the surface chemical analysis community.

AS-ThP-3 Effect of Soft X-Ray Beam on Channel Properties of 2D-Field Effect Transistor During *operando* X-ray Photoelectron Spectroscopy, ***Ansoon Kim***, *S. Choi,* Korea Research Instutue of Standards and Science (KRISS), Republic of Korea; *G. Oh, T. Kim,* Jeonbuk National University, Republic of Korea

"*Operando*", meaning under working conditions, analysis method has been developed to investigate the relationship between device performance and material properties. To examine chemical and electrical properties at the channel interface of thin film field-effect transistor (FET) under working condition, *operando* X-ray photoelectron spectroscopy (XPS) should be studied due to its surface-sensitive performance. Synchrotron radiation has been used for most *operando*-XPS studies [1,2] due to its good spatial resolution (~70 nm) compared to lab-based X-ray source (usually 10 µm). Nevertheless, synchrotron-based XPS has a limitation to perform *operando* analysis of soft materials because its high photon flux may cause sample damage. However, regarding 2D materials, in-depth researches about changes in chemical or electrical property induced by micro- or nano-focused X-ray have not been published despite of high demands and lots of interests for its *operando*-XPS studies.

In this presentation, we demonstrate whether there is a change in chemical and electrical properties of partially oxidized $MoTe_2$ and MoS_2 flakes induced by micro-focused lab-X-ray. In addition, we also verify whether the X-ray induced chemical changes can be accelerated by high gate voltage during conducting *operando* FET measurements. As a result of this study, we suggest a method to minimize the photon-induced damage for *operando*-XPS using lab-source that a lot of analytical researcher will use in the future.

[1] N. Nagamura et al, “Chemical potential shift in organic field-effect transistors identified by soft X-ray operando nano-spectroscopy,” *Appl. Phys. Lett.* **106**, 251604, 2015

[2] I. J. T. Jensen et al, “Direct Observation of Charge Transfer between NO_x and monolayer MoS_2 by Operando Scanning Photoelectron Microscopy,” *ACS Appl. Nano Mater.* **4**, 3319-3324, 2021

AS-ThP-4 Transient Grating Time-Resolved PEEM to Study Charge-Carrier Transport, ***Chandni Babu***, *D. Zigmantas,* Lund University, Sweden

Understanding the transport of charge carriers on surfaces enables us to get insights into a material's fundamental properties, which is also important from an application point of view. Time-resolved photoemission electron microscopy (TR-PEEM) has gained popularity in the study of ultrafast photocarrier dynamics in different materials. Here we present a novel approach for measuring the transport of photoexcited electrons at surfaces - transient grating time-resolved PEEM. In this approach, the sample is simultaneously excited by two pump pulses whose interference leads to a periodic spatial modulation of the excited electrons (1). These electrons are then photoemitted by the probe pulse and are imaged in the PEEM. The gradual decay of the spatial modulation due to transport processes can be observed, providing insights into diffusion and other transport phenomena over the short length and time scales. We are using this technique to study wurtzite InP platelets which is less explored than its thermodynamically stable counterpart- zinc blende InP. Understanding the transport properties of wurtzite InP will help in developing novel electronic and optoelectronic devices.

Reference

[1] Eichler, H.J., Günter, P., Pohl, D.W. (1986). Diffraction and Four-Wave Mixing Theory. In: Laser-Induced Dynamic Gratings. Springer Series in Optical Sciences, vol 50. Springer, Berlin, Heidelberg.

AS-ThP-5 Comparison of Commercially Available as-Received Lithium Metal Surfaces Using XPS and FTI, ***Harry Meyer***, *R. Sahore, A. Westover,* Oak Ridge National Laboratory

Lithium metal is used extensively a variety of battery applications. Like all alkali metals, Li-metal is reactive with ambient air to the point of being flammable. Li-metal must be stored in either vacuum or an inert atmosphere. The Department of Energy (DOE) sponsors a wide range of battery materials related projects because of their continued and growing importance to our society. One of these projects, sponsored by the Vehicle Technology Office (VTO) of DOE, is titled “Control of Li Surfaces for Solid-State Batteries”. In this project, our goal is to understand the role of native and engineered surface layers on the cycling behavior of lithium metal in solid-state batteries. An initial step of the project was to examine native surface layers of various commercial lithium which are used by most researchers in the field. Li-metal obtained from four commercial sources

was compared to Li-metal films prepared in our laboratory using thermal evaporation.

The as-prepared Li-metal film and the as-received Li-metal samples were stored in an inert Ar-filled glovebox prior to surface characterization using x-ray photoelectron spectroscopy (XPS) and Fourier transform infra-red spectroscopy (FTIR).FTIR analysis was done within the glovebox and so were never exposed to air. Samples for XPS were prepared in the Ar-filled glovebox by removing small sections from the as-received Li-metal materials and placing in a vacuum transfer holder (VTH). The VTH was sealed under vacuum in the load-lock of the glovebox, moved to the XPS laboratory, and unsealed by placing it in the vacuum load-lock of the XPS. The as-received surfaces were initially analyzed. Depth profiles were done to measure the composition as a function of depth. All samples showed a mix of Li-carbonate, Li-hydroxide, Li-oxide, and Li-carbide, but showed different distributions of each for each sample. This poster will compare the as-received surface compositions and compositions as a function of depth. This abstract has been authored by UT-Battelle, LLC under Contract No. DEAC05-00OR22725 with the U.S. Department of Energy.

AS-ThP-6 Silver and Aluminum by X-ray Photoelectron Spectroscopy (XPS)*, **Braxton Kulbacki**, S. Jafari, A. Dean, S. Ko, M. Linford,* Brigham Young University

Silver (Ag) and aluminum (Al) are important technological materials. They have also been extensively analyzed by x-ray photoelectron spectroscopy and other material characterization methods. Ag is used to calibrate the ThermoFisher K alpha XPS instrument. When calibrating the instrument using Ag, the 3d5/2 peak is placed at a binding energy of 368.21 eV. Calibration of the instrument should be performed every six months. In this poster, I show and discuss the Ag calibration peak (Ag3d5/2) as well as the Ag 3d3/2, Ag 3p3/2, Ag 3p1/2, Ag 3s, Ag 4p, Ag MNN and Ag survey scans. The sample for analysis was prepared by sputtering a silver surface. The C 1s, O 1s and Ar 2p scans are included in this poster to demonstrate both the low level of contamination and the presence of ion implanted Ar. As revealed in the C1s and O1s narrow scans, argon sputtering removed carbon and oxygen contamination from the silver surface. This poster will also show and discuss XPS of aluminum metal obtained by sputtering aluminum foil. The Al 2p peak will be shown, along with its peak fitting using asymmetric peaks that appropriately account for its spin-orbit splitting.

AS-ThP-7 Copper and Gold by X-ray Photoelectron Spectroscopy (XPS)*, **Annika Dean**, S. JAFARI, B. Kulbacki, S. ko, M. Linford,* Brigham Young University

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive analytical technique used to study the characteristics of different materials. We analyzed sputtered copper and gold using a ThermoFisher Scientific K-Alpha XPS instrument. Copper is often used in the calibration of XPS instruments, particularly the Cu $2p_{1/2}$ and Cu $2p_{3/2}$ peaks. The Au $4f_{7/2}$ peak is also used as a binding energy reference. While spectra for copper and gold are available using a variety of X-ray sources and instruments, the ThermoFisher Scientific K-Alpha XPS instrument is growing in use and popularity in the XPS community. As such, access to reference spectra taken with this instrument are an important resource. Elemental survey spectra are also useful for comparison when studying copper and gold-containing compounds, revealing changes in chemical and electronic states. Peak fitting of various signals is demonstrated, which suggests appropriate functional/mathematical forms for these signals.

AS-ThP-8 Xps Investigation of Monoatomic and Cluster Argon Sputtering of Zirconium Dioxide*, **Michael Burrell**,* Naval Nuclear Laboratory, Knolls Atomic Power Laboratory*; E. Gillman,* Naval Nuclear Laboratory, Bettis Atomic Power Laboratory

The surfaces of zirconium dioxide and yttria-stabilized zirconia (YSZ) have been analyzed using x-ray photoelectron spectroscopy (XPS) after ion sputtering with monoatomic Ar^+ or an argon gas cluster ion beam (GCIB). The O/Z ratio and new components in the Zr 3d lines show reduction to lower oxidation states when sputtered with monoatomic Ar^+, but significantly less damage is observed when GCIB sputtering is used. The damaged surface layer caused by Ar^+ sputtering can be removed by subsequent GCIB sputtering. However, the depth resolution observed in depth profiles of thin YSZ films was significantly better when Ar^+ sputtering is used. Differences in the Sn content in the oxidized Zr-4 specimen were also observed when comparing Ar^+ and GCIB sputtering, suggesting preferential sputtering. Interestingly, for YSZ the Y 3d lines showed no reduced species when sputtered with either source.

AS-ThP-10 Unlocking the Potential of Critical Rare Earth Minerals: Advanced Characterization and Analysis with XPS and RBS for Sustainable Resource Management*, **Sage Buchanan**,* Western University, Canada

As the only recognized critical mineral common to over 37 nations, rare-earth elements (REE's) have garnered increasing attention for their indispensable role in clean energy and sustainable modern living practices. As essential components of permanent magnets, light-emitting phosphors, catalytic converters, and various other materials, REE's underpin high-tech consumer electronics, green energy, and advanced medical and defense systems. The critical status of REE's stems from the growing demand for these applications, as well as the clear geopolitical significance threatening their supply chain. In order to maintain responsible resource management strategies and promote the sustainable use and disposal of REE's, it is crucial to have a comprehensive understanding of the properties and quality of REE-containing materials. In an effort to advance current methodologies surrounding the analysis and characterization of REE-containing materials, this work presents preliminary results from an in-depth X-ray Photoelectron Spectroscopy (XPS) and Rutherford backscattering (RBS) study on several REE-containing minerals of significance.

To establish robust characterization and analysis procedures, several standard samples of relevant REE-containing minerals such as monazite, bastnaesite, and xenotime, as well as the metals and their oxides will be examined via XPS. Comprehensive characterization and analysis procedures will be developed to serve as valuable reference data for future characterization of REE-containing materials. In parallel, RBS and photoluminescence studies will be utilized to develop known pure standards and investigate the depth distribution of REE implantations onto silicon wafers. Together, these techniques will provide a strong foundation for understanding the composition, electronic structure, and surface chemistry of these reference materials which can serve as benchmarks for future works and industrial applications. Understanding the role of REE's in these materials is critical for optimizing extraction and recycling processes, enhancing material performance, and identifying potential substitutes or alternatives if needed. This comprehensive approach will contribute to more efficient and sustainable use of REE's, alleviating geopolitical pressure while minimizing the environmental impact associated with the extraction and importation of REE's within and into North America.

AS-ThP-11 Computer-Readable Image Markers for Automated Registration in Correlative Microscopy*, **Peter Cumpson**,* University of New South Wales, Australia*; J. Sherriff,* University of Newcastle-upon-Tyne, UK

We present a newly developed methodology using computer-readable fiducial markers to allow images from multiple imaging modalities to be registered automatically. This methodology makes it possible to correlate images from many surface imaging techniques to provide an unprecedented level of surface detail on a nanometre scale that no one technique can provide alone.

This methodology provides the capability to navigate to specific areas of interest when transferring samples from machine to machine seamlessly. Then taking data acquired from scanning electron microscope (SEM), helium-ion microscopy (HIM), secondary ion mass spectrometry (SIMS), x-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and optical inspection tools and combining all the data acquired to then generate a 3D data representative model of a surface.

AS-ThP-12 Surface Restructuring and Stability of Perovskite Oxide Electrocatalysts Studied by Surface X-ray Diffraction and Grazing Incidence X-ray Absorption Spectroscopy*, **Alvin Chang**, R. Jana, K. Stoerzinger, Z. Feng,* Oregon State University

In recent years, the trend towards clean and renewable energy sources has led to an increased interest in water-based electrocatalysis (i.e., producing green hydrogen from water as fuels and chemicals) for energy conversion and storage, but a key barrier for efficient water splitting is the high overpotential of the sluggish oxygen evolution reaction (OER). To overcome this, earth-abundant perovskite oxides of chemical formula AMO_3 with compositional substitutions have shown drastically improved OER activities and are particularly attractive due to their high activity, low cost, high tunability of composition, and controllable electronic structures.For many metal oxides it was discovered that the surface can reconstruct under the oxidative conditions imposed by OER, forming (hydr)oxides prior to the onset of the reaction, and resulting in a different surface termination than

that expected from the bulk. This restructuring is varied among materials and plays a critical role in determining the stability and activity of an electrocatalyst material during and after electrochemical cycling. Thus, understanding the drivers of transformation at electrocatalyst interfaces towards the development of materials design is a key research direction in many fields. In this work we examine the impact of electrochemical cycling on surface reconstruction of Lanthanum Nickel Iron Oxide ($LaNi_{1-x}Fe_xO_3$:x=0-0.375) and Lanthanum Strontium Nickel Iron Oxide ($La_{0.5}Sr_{0.5}Ni_{1-x}Fe_xO_3$: x=0-0.625) epitaxial thin films. Surface X-ray diffraction (SXRD) is employed to investigate the relationship between complex oxide bulk composition and terminal surface OER activity and stability. X-ray reflectivity (XRR) is used to probe the electron density of surface layers and crystal truncation rod (CTR) is used to study atomic reconstruction at the surface. In select compositions, in-situ XRR and CTR illuminate the reconstruction and amorphization process during cycling under OER conditions. Furthermore, grazing incidence X-ray absorption spectroscopy (GIXAS) is performed to capture the evolution of local coordination environments with increasing compositional substitutions and soft XAS is used to explore local electronic structures. Our findings uncover the role of underlying bulk descriptors in modulating OER performance through cycling-induced restructuring and unearth the fundamental driving forces behind surface transformations in perovskite oxide materials which will provide invaluable understanding to aid in the development of electrocatalytic surfaces under OER conditions for effective materials design towards high-performance electrolyzers and batteries for renewable energy storage and conversion.

AS-ThP-13 XPS and ToF-SIMS Depth Profile Comparison of Si Heterojunction Solar Cells*, **Tae Kyong John Kim,***
Case Western Reserve University*; K. Davis,* University of Central Florida*; I. Martin,* Case Western Reserve University

X-ray Photoelectron Spectroscopy (XPS) is one of the most widely used analysis techniques for probing surface composition as well as the composition variation with depth (e.g. depth profile). Even though XPS offers quantitative analysis, limitations do exist when using the technique for depth profiling measurement of Si Heterojunction (SHJ) Solar Cells: probe depth (7-10 nm), detection limit (0.1 atomic %), peak overlaps, inability to measure Hydrogen. Such limitations can be overcome by utilizing another surface analysis technique: Time of Flight – Secondary Ion Mass Spectrometry (ToF-SIMS). ToF-SIMS offers a shallower probe depth (< 2 nm), more compatible with carrying out fine depth profile measurements (e.g. sputter segment of 2-3 nm); the technique also offers a higher detection limit (ppm-ppb), no peak overlap issue, and ability to measure Hydrogen. This work investigates the benefits and limitations of the two techniques when probing for differences in three SHJ Solar cells: Control, Good, Degraded. Even though XPS was able to monitor changes in Indium, Oxygen, and Silicon amounts, only ToF-SIMS was able to reveal the finer differences in the profiles of all of the elements considered (Sn, In, O, B, P, N, H): 1) Indium segregation at the ITO and a-Si:H interface, 2) difference in Boron distribution, 3) difference in the relative amounts of H, B, P, N.

AS-ThP-14 Surface Analysis of Ru and Ir Thin Films after Device Fabrication Processing Techniques*, **Randall Wheeler**, S. Antar, A. Valenti, C. Ventrice,*
SUNY Polytechnic Institute*; M. Strohmayer, J. Brewer, C. Nassar, C. Keimel,* Menlo Microsystems, Inc.

Microelectromechanical systems (MEMS) are micron scale devices with moving parts. In particular, MEMS devices can be used for radio frequency (RF) switches. Ruthenium is often used as the electrical contact material of these MEMS-based RF switches because of its resistance to oxidation at elevated temperatures. In addition, the most stable stoichiometry of ruthenium oxide is RuO_2, which is an electrically conductive oxide. As the power density of MEMS devices is increased, the rate of metal oxide formation on the surface of the metallic Ru contacts is expected to increase, which may adversely affect the performance of the device. Since iridium resists oxidation at high temperatures and also has an electrically conductive native oxide, it may be an alternative to Ru for higher temperature applications. Measurements have been made to determine the stoichiometry and thickness of the surface oxide on Ru and Ir films after typical semiconductor fabrication processing techniques such as reactive ion etch (RIE), plasma ashing processes, and annealing in air. The metal thin films are deposited on SiO_2/Si(100) substrates, and the primary analysis techniques used for this study are angle-resolved XPS and AFM.

AS-ThP-17 In-Depth Morphology/Evolution Characterization of an Obliquely Sputtered Micro/Mesoporous Si/SiO_2 Thin Film*, **Behnam Moeini,***
Department of Chemistry and Biochemistry, Brigham Young University*; D. Shollenberger, D. Bell,* Restek Corporation*; D. Fullwood,* Mechanical Engineering Department, Brigham Young University*; R. Vanfleet,* Department of Physics and Astronomy, College of Physical and Mathematical Sciences, Brigham Young Universit*; M. Linford,* Department of Chemistry and Biochemistry, Brigham Young University

In this study, we evaluate the morphology/evolution of obliquely sputtered micro/mesoporous Si/SiO_2 thin films. We utilize various microstructure characterization metrics relying on physical descriptors, and statistical functions (such as two-point correlation functions) to assess the films. Morphological analyses were performed on scanning transmission electron microscopy (STEM) images. To examine film evolution/growth, we employ contrast-enhanced STEM images. Prior to imaging, films were infiltrated with ZnO using atomic layer deposition (ALD). Our analysis of the two-point correlation function reveals a simple ellipse/spherical local pore geometry, which differs from the long-range irregular arrangement of pores. Furthermore, by analyzing the internal structure of the pores using homology metrics, we find a good correlation with the theoretical models of morphological evolution in obliquely sputtered films.

AS-ThP-18 Benefits of Cryo-XPS for Battery Analysis*, **Jonathan Counsell**, A.*
Roberts, Kratos Analytical Limited, UK*; C. Moffitt,* Kratos Analytical Inc., UK*; C. Blomfield,* Kratos Analytical Limited, UK*; D. Surman,* Kratos Analytical Inc.

Lithium-sulfur batteries (LSBs) are attractive because of their high theoretical energy density and low cost of raw materials. However, their commercialization has been hindered by several challenges, including the volume expansion of the sulfur electrode during cycling and the shuttle effect of polysulfide intermediates. To address these issues, it is crucial to have a deep understanding of the underlying mechanisms and the chemistry of the Li-S system.In the case of LSBs, XPS can be used to determine the oxidation states of sulfur and carbon in the anode material. Sulfur can exist in a range of oxidation states, from -2 to +6. The most commonly observed oxidation states of sulfur in LSBs are +2 and 0, corresponding to elemental sulfur and lithium sulfide, respectively. The presence of higher oxidation states, such as +4 and +6, can indicate the formation of polysulfide intermediates and the shuttle effect.The oxidation state of carbon can also be probed with XPS. Carbon can exist in various chemical environments, such as sp2 hybridized carbon in graphene-like structures or sp^3 hybridized carbon in amorphous carbon. The presence of sp2 hybridized carbon can indicate the formation of conductive carbon networks, which can improve electron transport and enhance the performance of the LSB.

However, it is important to note that XPS can also introduce spectral artefacts and alter the surface chemistry of the sample. XPS can cause damage to the sample surface, leading to the formation of new chemical species that may not represent the true surface chemistry. To mitigate these effects, cryo-XPS can be used, which involves cooling the sample to cryogenic temperatures during analysis. This can stabilize the surface and reduce the formation of artefacts, providing a more accurate representation of the true surface chemistry.

AS-ThP-19 Analysis of Buried Interfaces for Device Technology by Soft and Hard X-ray Photoelectron Spectroscopy*, **Jennifer Mann**, K. Artyushkova, S.*
Zaccarine, N. Biderman, Physical Electronics

Due to its accuracy and reliability in determining nm-thick overlayers on Si, X-ray photoelectron spectroscopy (XPS) has been utilized as a metrology technique for many years. Performing surface-sensitive XPS is more challenging with a soft X-ray source because the interfaces of interest are frequently hidden beneath metal electrodes or oxide layers.Higher energy X-ray beams have made it possible to detect photoelectron signals from deeper in the material, however most of this analysis was performed at sites with synchrotron radiation.The recent development of lab-based hard X-ray photoelectron spectrometers (HAXPES) has created new, accessible opportunities for routine analysis of technologically significant devices.

This poster will showcase the current state of the art and potential future directions for integrating HAXPES and XPS in the study of semiconductors and nanoelectronics. It will highlight the advantages of using hard X-ray sources with a lab-based high throughput fully automated spectrometer. These benefits include the ability to analyze buried interfaces, such as electronic layers located below a surface capping layer, and compositional studies in the bulk of materials and interfaces beyond the sampling depth of soft X-rays. Deeper sampling also reduces the impact of surface contamination on the photoelectron signal and enables exploration beyond

the potential depth of ion sputtering-induced damage. Additionally, eliminating the overlap between Auger and major photoemission peaks is crucial, particularly for transistor devices based on GaN technology, where quantification using XPS is impossible due to the overlap between Ga Auger peaks and N 1s photoelectron peaks.

Thin films of various types are critical components of modern microelectronic products. Conducting films form the interconnect layers in all chips, and dielectric films provide electrical insulation. Angle-resolved or angle-dependent XPS and HAXPES (ADXPS/ADHAXPES) is a powerful, non-destructive method that provides a quantitative chemical composition depth profile for thin film structures with thicknesses within the XPS sampling depth - under 5-10 nm for an Al K alpha soft X-ray source and ~15-30 nm for a Cr K alpha hard X-ray source. StrataPHI can be used for metrological applications in devices to estimate the structure of thin-film stacks from this angle-dependent data.

AS-ThP-20 X-ray Photoelectron Spectroscopy Analysis of PEMWE Catalyst Layers with Focus on Catalyst-Ionomer Interface*, **Jayson Foster,*** Colorado School of Mines, USA*; X. Lyu,* Oak Ridge National Laboratory, USA*; E. Padgett, S. Mauger,* National Renewable Energy Laboratory*; A. Serov,* Oak Ridge National Laboratory, USA*; S. Pylypenko,* Colorado School of Mines, USA

Polymer exchange membrane water electrolyzers (PEMWEs) are an increasingly attractive clean energy technology for producing H2 for transportation fuel. Low-temperature electrolysis systems need to make significant improvements in affordability, durability, and efficiency as well as in manufacturing scalability to meet the goal of decreasing the cost of clean hydrogen to $1/kg by 2030. Development of the next generation of PEMWEs depends on further improvements of the catalyst to achieve better activity and stability, and optimization of catalyst layer structure. This study focuses on investigating PEMWE catalyst layers with focus on catalyst-ionomer interface using x-ray photoelectron spectroscopy (XPS) as it is highly surface sensitive in identifying subtle chemical differences. XPS is a powerful technique for investigation of catalyst layers. We have previously demonstrated its ability to detect small variations in fuel cell catalyst layer composition as a function of various parameters, including catalyst ink composition and electrode fabrication. However, the ionomer is typically susceptible to X-ray induced damage during data acquisition, thus analysis was conducted with a recently developed procedure in an effort to mitigate instrumental artefacts. In this talk, we use XPS to determine spatial homogeneity of the catalyst layers to evaluate the quality of the coating methods and to compare composition of catalyst layers prepared by different fabrication methods. Next, XPS is used to probe small variations in catalyst layer composition as a function of ink shelf life. And finally, differences in the catalyst layer composition are evaluated as a function of durability testing conditions. Across these studies, elemental ratios of F to Ir were used to quantitatively track surface ionomer content relative to the amount of IrO2 nanoparticles. Additionally, peak fitting of the O 1s spectrum was analyzed to provide further perspective on the catalyst-ionomer interface composition. This talk emphasizes the capabilities of XPS to advance our understanding of the catalyst-ionomer interface as related to catalyst ink properties, catalyst layer manufacturing, and catalyst layer durability.

AS-ThP-21 Correlative ToF SIMS and STEM-EDS Analysis of Platinum Coatings on Electrolyzer Porous Transport Layers*, **Genevieve Stelmacovich,** L. van Eijk, M. Coats,* Colorado School of Mines*; S. Ware, J. Young,* National Renewable Energy Laboratory*; M. Walker,* Colorado School of Mines*; G. Bender,* National Renewable Energy Laboratory*; S. Pylypenko,* Colorado School of Mines

As the United States energy infrastructure moves towards integration of a hydrogen economy, advancing electrolyzer and fuel cell technologies has become increasingly important. In Proton Exchange Membrane Water Electrolyzers (PEMWE's), the anode catalyst layer (CL), the porous transport layer (PTL), and the interface between these two layers require further optimizations. To improve this interface and mitigate degradation involving oxide formation, titanium based PTLs are typically coated with a thin protective coating, usually platinum. It is essential to characterize PTL coatings and the CL/PTL interface to ensure limited platinum use while mitigating degradation effects.

We have recently demonstrated the capabilities of ToF SIMS as a characterization technique for PTLs, specifically its ability to differentiate coatings with different thicknesses and identify titanium and platinum oxide species at the CL/PTL interface through depth profile analysis. However, quantification of coating and oxide thickness is hindered due to the morphological nature of these materials as well as lack of standards. Our recent work focuses on correlations between Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and Scanning Transmission Electron MicroscopyEnergy-dispersive X-ray Spectroscopy (STEM-EDS) results for a series of Pt-coated samples with varied thicknesses of platinum. The same amount of time was used to coat flat titanium substrates and felt PTLs, providing samples with a range of coating thicknesses. Samples were cross-sectioned with Focused Ion Beam Scanning Electron Microscopy (FIB-SEM) for STEM-EDS analysis to determine thickness of Pt coatings and assess layer morphology. ToF-SIMS measurements were conducted on the same samples to obtain depth profiles, comparing measurements from three locations on each sample to understand the reproducibility of ToF-SIMS measurements and correlate them with TEM-EDS data. This talk will discuss reproducibility, sputter rates, and depth profile time conversions along with future directions of ToF SIMS on PTLs for investigation of degraded samples.

AS-ThP-22 Using X-Ray Photoelectron Spectroscopy (XPS) to Characterize Organo-Mineral Complexes in Environmental and Synthesized Samples*, **Qian Zhao**, M. Engelhard, A. Bhattacharjee,* Pacific Northwest National Laboratory*; E. Rooney,* University of Tennessee, Knoxville*; E. Herndon,* oak Ridge Natinal Laboratory*; K. Bidas,* University of Tennessee, Oak Ridge National Laboratory

X-ray photoelectron spectroscopy (XPS) analysis is a powerful surface characterization approach to understanding the most dynamic interface of a material. The understanding of the interface of organics and minerals in soil is critical to global carbon (C) cycling as minerals play an important role in persisting soil organic matter (SOM). Yet mechanisms of the accumulation of organic matter (OM) by associating with minerals in soil are still unclear. Chemical characterization of OM that associate with minerals provides a mechanistic understanding of mineral-OM interactions. Surface characterization, such as XPS, allows us to probe the chemical states and speciation of OM on the surface of mineral particles. This work used both synthetic mineral-OM complexes and natural soil samples to investigate the chemistry of organics that associate with minerals. In the synthetic system, we employed synthetic soil habitat (SSH) platform that can simulate soil pore distribution and mineralogy, to probe OM-mineral interactions under changing biogeochemical conditions. Surface of SSH pores was pre-coated with ferrihydrite. Water extracted OM from soil flow through the SSH platform. Surface of SSH was measured before and after OM sorption by using XPS. XPS analysis found the relatively higher concentration of C in ferrihydrite-coated surface than control. Further, the deconvolution of C 1s spectra reveals that certain carbon functional groups of SOM are preferentially adsorbed to ferrihydrite-coated surfaces. In the soil system, mesh bags (5 µm) containing ferrihydrite-coated quartz, hydrous Mn oxide-coated quartz, or quartz were buried in Toolik surface soils and incubated for 7, 14, and 28 days. The incubated mineral bags were analyzed via XPS to evaluate the quantity and composition of OM compounds that associate with specific minerals as well as spatially resolved changes in Fe and Mn speciation. We found higher organic contents in ferrihydrite-coated sand than Mn and quartz. The XPS data generated by the SSH experiments and Toolik buried mineral bag analyses are combined to provide a cross-scale understanding of organo-mineral interactions that develop in thawing permafrost soils under both redox conditions and increasing frequency of freeze-thaw cycles.

AS-ThP-23 Do Different XPS Systems Give the Same Result?*, **Lyndi Strange**, D. Baer, M. Engelhard, V. Shutthanandan,* Pacific Northwest National Laboratory*; A. Shard,* National Physical Laboratory, U.K.

Analyses of the literature indicate that there is growing use of XPS in multiple fields of research, and also a growing amount of faulty data analysis appearing in the literature. With the increasing number of XPS users, it is important that significant detail is paid toward data acquisition and analysis to ensure reproducible results. In our laboratory we have instruments from three vendors. Sometimes it is necessary to collect data from the instrument that is available at the time the analysis is needed. In addition, users often take the data away and analyze it using a variety of software packages. It is useful to know if data collected on "identical" samples produces the same results when collected on different systems and using "native" and other software packages for analysis. This paper describes a simple test of data collection on three different systems and analysis using the "native" software for each system and analysis when naively exported to CasaXPS.Our simple test sample was cleaned copper foil for onwhich we collected survey spectra and high-energy resolution Cu 3p and Cu 2p data using Kratos Axis DLD Ultra, Thermo-Fischer NEXSA, and Phi Quantera spectrometers. The following analyses and data comparison were conducted for both survey and narrow window data: i) comparison of

Cu 3p and Cu 2p peak ratios, ii) Cu 3p and Cu 2p atom ratios using native software and iii) when exported to CasaXPS. In addition, we compared the full survey spectra shapes to the ideal Cu spectra provided by the National Physical Laboratory. We note that many software packages apply transmission function correction information to peak areas during analysis, not to collected data (although the NEXSA has an option of doing it either way). Good news is that using recently calibrated instruments and vendor supplied sensitivity factors, when the analysis is done consistently – using iterated Shirley background between 58.0 and 91.0 for the Cu 3p and 920.0 eV to 970.0 eV for the Cu 2p - the same quantity of Cu is indicated to better than 3% With attention to information transfer including transmission function information, and use of appropriate consistent sensitivity factors, similar results when using CasaXPS analysis.Thus, excellent consistency can be obtained in comparing data from different systems. However, consistent reporting of the steps needed for consistent data analyses are often not reported in publications thus the quality and consistency of the analyzed data is often unknown or incorrect.

AS-ThP-25 Correlative Microscopy of SIMS, Helium Ion Microscopy and XPS, ***Jake Sheriff***, *I. Fletcher,* Newcastle University, UK*; P. Cumpson,* University of New South Wales, Australia

Secondary ion mass spectrometry (SIMS) is a widely used surface analytical technique to interpret surface composition. As a primary beam is raster-scanned across a surface it is possible to recreate a total ion image from the secondary ions ejected [1]. The Ionoptika J105 is equipped with two ion beams; C60 and GCIB, the resolution of the images generated by the J105 is dictated by the spot size of these beams.

The Helium ion microscope (HIM) developed by Zeiss uses a beam of He ions to generate a secondary electron image of a surface. The use of He ions as the imaging beam allows for a spot size down to <0.5nm [2]. This has allowed the HIM to take high resolution images on a submicron scale. Unusually, at Newcastle we use a magnetic-sector analyser to allow SIMS mapping of the surface as pioneered by LIST [3], giving potentially the highest spatial resolution of any SIMS instrument.

The Axis Nova X-ray photoelectron spectrometer (XPS) is capable of parallel imaging. This is done by illuminating the sample surface with x-rays then either electrostatically of magnetically projecting the electrons into the detector [4]. Using this type of imaging one can acquire a quantifiable image of the elemental distribution from a sample's surface.

All of these techniques only tell a part of a surface's story. The HIM is able to show an accurate picture of surface morphology with nanometre resolution, while the SIMS is able to give the composition of the surface at the submicron scale and XPS can quantify the elemental distribution. By combining these techniques one can put these parts together and gain a better understanding of the surface structure, be it a bacterial colony or a piece of Martian rock.

We have developed a methodology to be able to co-localise areas of interest when transferring samples between multiple different surface techniques. Then automatically correlate all the images to form an accurate representation of a surface [5]. Correlative microscopy with SIMS, XPS, and HIM, allows an unprecedented level of surface detail to be found.

References

[1] J.C. Vickerman et al, *Surface Analysis The Principal Techniques*, 113-199, 2009

[2] D.C. Joy *Helium Ion Microscopy Principles and Applications*, 9-15, 2013

[3] T Wirtz *et alNanotechnology*26, 434001, 2015

[4] P. Van der Heide *X-ray Photoelectron Spectroscopy An introduction to Principles and Practices*, p54-56 2012

[5] J. Sheriff, *Ultramicroscopy", 228, 113322, 2021*

AS-ThP-27 The Utility of Surface-Induced Dissociation in Molecular Identification, ***Gregory L. Fisher,*** Physical Electronics*; S. Iida,* ULVAC-PHI, Japan

Kilo-electron volt collision-induced dissociation (keV-CID) enables the compositional identification and structural elucidation of molecules, metabolites and degradation products with 2D/3D visualization by mass spectrometry imaging (MSI). TOF-SIMS tandem MS imaging has been brought to bear for unambiguous molecular visualization in single cell-omics [1], natural product chemistry [2], metabolomics [3,4], surface modification [5], biocompatibility, high performance polymers and composites [6], 2D materials [7], electronic devices [8], catalysis [9], forensic and failure analysis, bio-medicine and pharmaceuticals [10-12]. Here, we will introduce and explore the advantages of surface-induced dissociation (SID) to assist molecular identifications together with the CID spectra. In contrast to the CID which promotes cleavage at every molecular bond, the SID is more subtle in that the bond cleavages result predominantly in the observation of functional group chemistry. While the SID and CID are generated at the same kinetic energy, the molecular energetics are distinct which can have a pronounced effect on the calibration and, hence, the putative peaks used for precursor identification.

References

[1] C.E. Chini, et al, *Biointerph*. **13** (2018) 03B409.

[2] A. Mikhael, et al, *Rapid Comm. Mass Spectrom*. (2020) DOI: 10.1002/rcm.8740.

[3] T. Fu, et al, *Anal. Chem*. **90** (2018) 7535-7543.

[4] T. Fu, et al, *Nat. Sci. Rep*. **9** (2018) 1928-1938.

[5] G.L. Fisher, et al, *Anal. Chem*. **88** (2016) 6433-6440.

[6] S. Iida, et al, *Bunseki***2018(2)** (2018) 52-57 (Japanese).

[7] G.L. Fisher, et al, *Microscop. Microanal*. **23** (2017) 843-848.

[8] S. Iida, et al, *Rapid Comm. Mass Spectrom*. (2019) DOI: 10.1002/rcm.8640.

[9] S. Oh, et al, *Chem. Mater*. **32** (2020) 8512-8521.

[10] A.L. Bruinen, et al, in Imaging Mass Spectrometry: Methods and Protocols, L.M. Cole, Ed. (Springer, 2017) p. 165-173.

[11] N. Ogrinc Potočnik, et al, *Anal. Chem*. **89** (2017) 8223.

[12] Y. Shi, et al, *J. Proteome Res*. **18** (2019) 1669-1678.

AS-ThP-28 Unraveling the Temperature Induced Phase Transitions of Pbo_x Using Multi-Modal Characterization Approach, ***Ajay Karakoti,*** *V. Shutthanandan, D. Bazak, D. Nguyen, V. Murugesan,* Pacific Northwest National Laboratory

Lead acid batteries are one of the oldest commercial batteries that have proven their reliability over the years in multiple battery applications such as starting-lighting-Ignition (SLI) batteries, uninterruptible power supply(UPS), and emergency lighting etc. Despite its extensive use, limited research work in this battery technology have culminated into several research challenges that must be resolved for the further progression of this battery technology. Oxygen vacancy mediated transition of PbO_x phases (of varying stoichiometry) during electrode fabrication and during the charge-discharge process is one such unresolved problems that have perplexed the researchers for many years. Prior investigations of the PbO_x phase evolution during thermal processing using spectroscopic and diffraction methods have shown that PbO_2-Pb_3O_4 transition passes through multiple stages though the exact stoichiometry and composition of the transition phases have never been fully understood. This study uses multimodal characterization approach to identify the structure and composition of PbO_x phases during the thermally induced phase transitions. Combined high temperature X-ray photoelectron Spectroscopy (XPS) and residual gas analysis (RGA) showed that initial surface of PbO_2 is oxygen deficient, and that Pb oxidation state changes concurrently with oxygen release during heating. It is found that the oxygen evolution and corresponding oxidation state changes occur in continuous manner instead of demonstrating a transition at fixed temperature as observed using thermogravimetry analysis. XPS and RGA analysis also reveal that the phase transition can occur at a relatively lower temperatures in high vacuum conditions revealing a potential of vacuum and beam induced damage in Pb-based materials. The talk will also highlight the challenges in the quantitative XPS analysis of lead samples. Complimentary information from different characterization techniques such as Raman and NMR spectroscopy was combined to understand the thermally induced phase transition of PbO_x that could potentially relate to the evolution of PbO_x phases observed in lead acid batteries.

AS-ThP-29 Quantitative Investigation of SiP and SiGe Layers using HAXPES and ToF-SIMS, *N. Gauthier,* ***Olivier Renault****, E. Martinez, J. Barnes, J. Richy, J. Kanyandekwe,* CEA-LETI, France

Nowadays, "more Moore" and "more than Moore" device architectures have strongly increased the importance of novel materials thereby necessitating the availability of adequate characterization and metrology for reliable process control. For instance, the introduction of SiGe or SiP compounds used in MultiChannel Field Effect devices or raised sources and drain leads to the need for the determination of the exact composition of the resulting films. In this work, the quantification of binary materials such

as SiP and SiGe has been investigated using mainly non-destructive HAXPES and ToF-SIMS. Indeed, while the main obstacle to the use of RBS is the characterization of thin films, techniques with appropriate quantification capabilities like Atom Probe Tomography and Transmission Electron Microscopy are both time consuming and suffer from a lack of sensitivity due to their highly localized analysis volume. For quantitative characterization, the conventional X-ray Photoelectron Spectroscopy (XPS) is a powerful tool. Yet, its low analysis depth remains a major limiting factor to study buried interfaces and especially in this study, since the obtained Si-based layers are oxidized in ambient conditions (or because they should be protected by metallic layers of a few nanometers). A novel lab-based hard x-ray sources (HAXPES) was used to investigate both the chemical composition at the binary material surface and the in-depth distribution of SiO_2 within the layer thanks to the increase of the inelastic mean free path of electrons with increasing photon energy (Chromium Kα, *hv* = 5414.7 eV) [1]. To confirm the composition of the materials of interest obtained by HAXPES measurements and to calculate the adequate relative sensitive factor (RSF), the same films were characterized by ToF-SIMS. However, such as for HAXPES, Secondary Ion Mass Spectrometry (SIMS) characterization of SiP/SiGe layers often suffers from matrix effects due to the non-linear variation of ionization yields with P/Ge content. This limitation can be surpassed by analyzing reference samples, by following MCs^{2+} secondary ions or using the full spectrum protocol [2]. Finally, the P and Ge (Si) compositions of the secondary ion beam were calculated and compared with the reference composition as determined by X-ray Diffraction. The repeatability of the measurements and the influence of the layer oxidation were also studied. To conclude, the in-depth composition of the layers and the thickness of surface oxide were accurately evaluated by coupling the HAXPES results with ToF-SIMS.

[1] O. Renault et al., *Faraday Disc*. **236**, 288-310 (2022).

[2] M. Py, et al., Rapid Commun. Mass Spectrom. 2011, 25, 629–638

AS-ThP-30 Tof-SIMS Analyses in an H_2 Atmosphere: Improvements in Thin Films Depth Profiling and Reduction of Matrix Effect*, J. Ekar,* ***Janez Kovač,***

Jozef Stefan Institute, Slovenia

ToF-SIMS is a very versatile and widely applicable method for precisely characterizing the molecular structure of surfaces. Still, it also has limitations, like nonquantitative analysis caused by the matrix effect, which limits the capabilities of depth profiling of thin films. Namely, chemically similar layers are challenging to distinguish in SIMS depth profiling of thin films, and interfaces between them are difficult to identify. The reason for this is a change in the ionization yields caused by chemical composition varying from layer to layer. However, there are different ways of reducing the matrix effect. Most widely applied are laser or electron beam post ionization (SNMS), metal-assisted and matrix-enhanced SIMS, dynamic reactive ionization (DRI), and the introduction of different gases into the analysis chamber (gas flooding).

We applied the gas flooding approach to reduce the matrix effect and improve ToF-SIMS depth profiling, testing different atmospheres such as H_2, C_2H_2, CO, and O_2 in the 10-5 Pa pressure range during the analysis [1]. Gas flooding with O_2 was previously used, while our group introduced the other three gases as a novelty. We achieved the best results with the H_2 gas flooding during SIMS dual beam depth profiling. H_2 atmosphere enables more straightforward and unambiguous differentiation of thin layers of metals (Cr, Al, Ti, Fe, Ni, Ag) and their oxides, different metals, and alloys with different compositions. Furthermore, the identification of interfaces becomes easier. We also did not observe a change in the sputter rate during H_2 flooding. Surface roughening caused by the ion bombardment during depth profiling was also reduced in the H_2 atmosphere [2]. This effect is more evident after longer sputtering and depends on the chemical composition of the layer of interest. We assume that this is due to surface amorphization during the sputtering process. Our recent SIMS results also show a correlation between the SIMS signals from metals in alloys when comparing alloys with different chemical compositions analyzed in the H_2 atmosphere. The O_2 atmosphere also gives better results than UHV conditions, but improvement is less pronounced than in the case of H_2 flooding. These findings bring ToF-SIMS one step closer to becoming at least a semiquantitative method for surface chemical characterization.

[1] J. Ekar, P. Panjan, S. Drev, J. Kovač. ToF-SIMS Depth Profiling of Metal, Metal Oxide, and Alloy Multilayers in Atmospheres of H_2, C_2H_2, CO, and O_2. *J. Am. Soc. Mass Spectrom.* 2022, *33*, 31– 44.

[2] J. Ekar, J. Kovač. AFM Study of Roughness Development during ToF-SIMS Depth Profiling of Multilayers with a Cs^+ Ion Beam in a H_2 Atmosphere. *Langmuir* 2022, *38*, 12871–12880.

AS-ThP-34 Analysis of Defective Electrical Characteristics of Metal-Insulator-Metal(Mim) Capacitor and Improvement of Leakage Characteristics*,* ***SUNG Gyu PYO,*** CAU, Republic of Korea

One of the most important characteristics required for RF capacitors is the minimization of the parasitic factor. The representative parasitic factor is the series resistance and the parasitic capacitance between the Si substrate and the MIM (Metal-Insulator-Metal) capacitor that can minimize this. Most compound semiconductors are equipped with MIM capacitors, and there is a trend to adopt MIM capacitors in the CMOS process. In general, when applying a PIP (Poly SiInsulator-Poly Si) capacitor, the distance from the Si substrate is 3000 to 5000 Å, and the parasitic capacitance accounts for 10 to 20% of the total capacitance, and is responsible for poly depletion at the interface between the insulator and the poly electrode. The voltage coefficient of the capacitance is also bad. Additionally, it is difficult to secure a high quality factor due to the parasitic resistance factor of Poly Si. Therefore, to overcome these problems, MIM capacitors using metal electrodes are being introduced. MIM capacitor uses a metallization layer with low resistance and no depletion as an electrode, so it can realize a high quality factor by greatly reducing the parasitic capacitance factor with the Si substrate. In the Al-based metal structure (Ti/Al/Ti/TiN or Ti/TiN/Al/Ti/TiN), siliconnitride has better interface characteristics with the metal electrode than silicon dioxide, so it can maintain stable capacitance, has low voltage dependence, and has low leakage. Current characteristics are also relatively good. In addition, compared to silicon nitride, the thickness of silicon dioxide to secure the same level of capacitance density is relatively thin, so the proportion of changes in interface properties or property degradation at pattern edges increases, so in terms of pattern size dependence, silicondioxide In the case of the MIM top electrode etch process, dummy metal cannot be inserted during MIM patterning, so the pattern density is very low (~0.1%), and the topelectrode etch condition has good etch uniformity and a large selectivity for thin Si3N4 films. Selection of the EPD (End Point Detection) signal and appropriate etch target is different for each reticle, so target control is not easy. Because metal-rich polymer occurs due to low pattern density, it is not easy to optimize post-processing conditions. In this study, we would like to present research results on the evaluation of electrical characteristics in this MIM structure and the influence and improvement of leakage current characteristics.

AS-ThP-35 Assessment of Hafnium Oxynitride ($HfO_{1-x}N_x$) and Silicon Hafnium Oxynitride ($SiHfO_{1-x}N_x$) Components in Hf 4f XPS Spectra*, M. Mayorga Garay,* CINVESTAV-Queretaro, Mexico*; J. Torres Ochoa,* Universidad Politecnica de Juventino Rosas, Mexico*; O. Cortazar Martinez,* ***Dulce Maria Guzman Bucio****, A. Herrera Gomez,* CINVESTAV-Unidad Queretaro, Mexico

Nitrided hafnium oxide is employed in CMOS devices. Annealing causes species migration and the growth of interface layers. A proper characterization of the chemical composition and depth profile of this type of multilayered nanofilms is essential; ARXPS is the tool of choice.

Using ARXPS, we characterized and explored the limits on hafnia nitridation through remote plasma. Hf 4*f*, Si 2*p*, O 1*s*, C 1*s*, and N 1*s* spectra were acquired before and after nitridation with various plasma power levels (500 W-2500 W). We discriminated the peak components using advanced tools such as Active Background and Simultaneous Fitting, both encompassed in the fitting software AAnalyzer®.

The Si 2*p* spectrum before nitridation shows a signal at 102.47 eV which is attributed to $Si_{1-w}Hf_wO_2$ with high hafnium content. A byproduct of nitridation is oxidation of the substrate; a peak related to SiON appears at 102.65 eV. The Si 2*p* peak in $Si_{1-w}Hf_wO_2$ shifts to lower binding energies after plasma treatment due to dipole effects. Silicon content increases in $Si_{1-w}Hf_wO_2$ and one overlapped contribution related to $Si_{1-w}Hf_wO_{2-z}N_z$ appears. Before nitriding, the Hf 4*f* spectra show peaks related to HfO_2 (17.3 eV) and $Si_{1-w}Hf_wO_2$ (17.8 eV). After nitriding, the fitting revealed two extra signals at 16.8 and 16.38 eV which are attributed to $SiHfO_{1-x}N_x$ and $HfO_{1-x}N_x$.

AS-ThP-36 A Novel Approach for Discriminating Cu^0 and Cu^{1+} in Cu 2*P* Photoemission Spectra

A. Torres-Ochoa, Universidad Politecnica Juventino Rosas, Mexico*; D. Cabrera-German,* Universidad de Sonora, Mexico*; O. Cortazar-Martinez,* CINVESTAV-Unidad Queretaro, Mexico*; M. Bravo-Sanchez,* Universidad de Guadalajara, Mexico*; G. Gomez-Sosa,* ***Alberto Herrera-Gomez****,* CINVESTAV-Unidad Queretaro, Mexico

The photoemission spectra of Cu 2*p* have been extensively examined because of the numerous uses of copper in electronics and catalysis. The Cu 2*p* spectra pose a particular challenge primarily since the Cu^0 and Cu^{1+} peaks overlap and share almost identical shapes and are hard to distinguish by eye or peak-fitting analysis. Cu^{1+} and Cu^{2+} often coexist. This study reveals a subtle yet significant difference in the primary signal of the Cu $2p_{1/2}$ branch. The variation in the Lorentzian width of the Cu $2p_{1/2}$ branch enables the assessment of relative concentrations of Cu^0 and Cu^{1+}. To achieve this level of analysis, advanced fitting techniques were employed, including the Block Method, Active Background, and SVSC background. The use of these tools allowed for closely fitting all the photoemission spectra. Through precise peak-fitting analysis, it was possible to quantify the relative ratio of Cu^{1+} to Cu^0 states regardless of their significant overlap and the presence of Cu^{2+} signal.

AS-ThP-37 Morphological and Chemical State Characterization of CuO Nanoparticles and Thin Films

M. Kazi Hanium, Department of Physics, University of Dhaka, Bangladesh*; S. Rodriguez Bonet, M. Bosco,* ***Florencia Carolina Calaza,*** Instituto de Desarrollo Tecnológico para la Industria Química, Argentina

In recent years, transition metal oxides thin films have gained a great attention from material scientists and engineers due to their different properties which in turn provide promising applications in various fields of technology. Cu_xO has beenidentified as promising materials for solar energy conversion. In addition to their favorable band gap energies that allow for the utilization of visible light, the low cost, earth abundance, and non-toxicity of Cu are additional advantages for developing Cu-based photoelectrodes However, the poor-stability problem in the aqueous solution and low efficiency of Cu_xO thin films limit their final applications. The performance of the copper oxide thin films can be enhanced by improving the crystal quality and surface morphology of the material. Among different synthesis strategies for thin film fabrications, solution-processed methods, such as hydrothermal and electrophoretic deposition, are attractive in terms of their scalability, financial advantages and eco-friendliness. This work aims to provide a critical picture of the synthesis of Cu_xO thin films and nanoparticles by solution-processed methods. Precisely controlling the synthetic strategies will be our main focus which hopefully can contribute some useful information that helps to better understand the relation between synthetic process, final morphology, and the properties of corresponding Cu_xO thin films. In summary, results will be presented for CuO nanoparticle synthesis where the materials were calcined at different temperatures ranging from 300 to 500 C, showing mainly CuO chemical composition and structure, but a hint to the presence of Cu_2O on the surface is observed by CO IR titration experiments. In the case of thin films deposited on glass by spin coating methods from copper chloride solutions, and then annealed to 300 and 400 C, CuO micro sized needles are obtained but the presence of Cl ions is unavoidable even at the highest temperature of calcination.

Author Index

Bold page numbers indicate presenter

— A —
Antar, S.: AS-ThP-14, 3
Artyushkova, K.: AS-ThP-19, 3
Auerbach, D.: AS-ThP-1, 1
— B —
Babu, C.: AS-ThP-4, **1**
Baer, D.: AS-ThP-23, 4
Barnes, J.: AS-ThP-29, 5
Bazak, D.: AS-ThP-28, 5
Bell, D.: AS-ThP-17, 3
Bender, G.: AS-ThP-21, 4
Bhattacharjee, A.: AS-ThP-22, 4
Bidas, K.: AS-ThP-22, 4
Biderman, N.: AS-ThP-19, 3
Blomfield, C.: AS-ThP-18, 3
Bosco, M.: AS-ThP-37, 7
Bravo-Sanchez, M.: AS-ThP-36, 7
Brewer, J.: AS-ThP-14, 3
Buchanan, S.: AS-ThP-10, **2**
Burrell, M.: AS-ThP-8, **2**
— C —
Cabrera-German, D.: AS-ThP-36, 7
Calaza, F.: AS-ThP-37, **7**
Campbell, C.: AS-ThP-1, 1
Chang, A.: AS-ThP-12, **2**
Choi, M.: AS-ThP-2, 1
Choi, S.: AS-ThP-2, 1; AS-ThP-3, 1
Coats, M.: AS-ThP-21, 4
Cortazar Martinez, O.: AS-ThP-35, 6
Cortazar-Martinez, O.: AS-ThP-36, 7
Counsell, J.: AS-ThP-18, **3**
Cumpson, P.: AS-ThP-11, **2**; AS-ThP-25, 5
— D —
Davis, K.: AS-ThP-13, 3
Dean, A.: AS-ThP-6, 2; AS-ThP-7, **2**
— E —
Ekar, J.: AS-ThP-30, 6
Engelhard, M.: AS-ThP-22, 4; AS-ThP-23, 4
— F —
Feng, Z.: AS-ThP-12, 2
Fisher, G.: AS-ThP-27, **5**
Fletcher, I.: AS-ThP-25, 5
Foster, J.: AS-ThP-20, **4**
Fullwood, D.: AS-ThP-17, 3
— G —
Gauthier, N.: AS-ThP-29, 5
Gillman, E.: AS-ThP-8, 2
Gomez-Sosa, G.: AS-ThP-36, 7
Guzman Bucio, D.: AS-ThP-35, **6**
— H —
Herndon, E.: AS-ThP-22, 4
Herrera Gomez, A.: AS-ThP-35, 6
Herrera-Gomez, A.: AS-ThP-36, **7**
Hwang, H.: AS-ThP-2, 1
— I —
Iida, S.: AS-ThP-27, 5
— J —
Jafari, S.: AS-ThP-6, 2
JAFARI, S.: AS-ThP-7, 2
Jana, R.: AS-ThP-12, 2
— K —
Kanyandekwe, J.: AS-ThP-29, 5
Karakoti, A.: AS-ThP-28, **5**
Kazi Hanium, M.: AS-ThP-37, 7
Keimel, C.: AS-ThP-14, 3
Kim, A.: AS-ThP-2, 1; AS-ThP-3, **1**
Kim, J.: AS-ThP-2, **1**
Kim, T.: AS-ThP-13, **3**; AS-ThP-3, 1
ko, S.: AS-ThP-7, 2
Ko, S.: AS-ThP-6, 2
Koch, N.: AS-ThP-2, 1
Kovač, J.: AS-ThP-30, **6**
Kulbacki, B.: AS-ThP-6, **2**; AS-ThP-7, 2
— L —
Lee, K.: AS-ThP-2, 1
Linford, M.: AS-ThP-17, 3; AS-ThP-6, 2; AS-ThP-7, 2
Liu, F.: AS-ThP-2, 1
Lyu, X.: AS-ThP-20, 4
— M —
Mann, J.: AS-ThP-19, **3**
Martin, I.: AS-ThP-13, 3
Martinez, E.: AS-ThP-29, 5
Mauger, S.: AS-ThP-20, 4
Mayorga Garay, M.: AS-ThP-35, 6
Meyer, H.: AS-ThP-5, **1**
Moeini, B.: AS-ThP-17, **3**
Moffitt, C.: AS-ThP-18, 3
Murugesan, V.: AS-ThP-28, 5
— N —
Nassar, C.: AS-ThP-14, 3
Nguyen, D.: AS-ThP-28, 5
— O —
Oh, G.: AS-ThP-3, 1
— P —
Padgett, E.: AS-ThP-20, 4
Park, Y.: AS-ThP-2, 1
Pylypenko, S.: AS-ThP-20, 4; AS-ThP-21, 4
PYO, S.: AS-ThP-34, **6**
— R —
Renault, O.: AS-ThP-29, **5**
Richy, J.: AS-ThP-29, 5
Roberts, A.: AS-ThP-18, 3
Rodriguez Bonet, S.: AS-ThP-37, 7
Rooney, E.: AS-ThP-22, 4
— S —
Sahore, R.: AS-ThP-5, 1
Serov, A.: AS-ThP-20, 4
Shard, A.: AS-ThP-23, 4
Sheriff, J.: AS-ThP-25, **5**
Sherriff, J.: AS-ThP-11, 2
Shin, D.: AS-ThP-2, 1
Shollenberger, D.: AS-ThP-17, 3
Shutthanandan, V.: AS-ThP-23, 4; AS-ThP-28, 5
Stelmacovich, G.: AS-ThP-21, **4**
Stoerzinger, K.: AS-ThP-12, 2
Strange, L.: AS-ThP-23, **4**
Strohmayer, M.: AS-ThP-14, 3
Surman, D.: AS-ThP-18, 3
— T —
Torres Ochoa, J.: AS-ThP-35, 6
Torres-Ochoa, A.: AS-ThP-36, 7
— V —
Valenti, A.: AS-ThP-14, 3
van Eijk, L.: AS-ThP-21, 4
Vanfleet, R.: AS-ThP-17, 3
Ventrice, C.: AS-ThP-14, 3
— W —
Walker, M.: AS-ThP-21, 4
Ware, S.: AS-ThP-21, 4
Westover, A.: AS-ThP-5, 1
Wheeler, R.: AS-ThP-14, **3**
— Y —
Young, J.: AS-ThP-21, 4
— Z —
Zaccarine, S.: AS-ThP-19, 3
Zhao, K.: AS-ThP-1, **1**
Zhao, Q.: AS-ThP-22, **4**
Zhao, Z.: AS-ThP-2, 1
Zigmantas, D.: AS-ThP-4, 1