Monday Afternoon, November 7, 2022

Applied Surface Science Division
Room 320 - Session AS+CA+EL+EM+LS+SE+SS-MoA

Quantitative Surface Analysis

Moderators: Jordan Lerach, PPG Industries, **Hong Piao**, FUJIFILM Electronic Materials USA., Inc.

1:40pm **AS+CA+EL+EM+LS+SE+SS-MoA-1 Hard Targets: Developing Tools for Quantitative HAXPES*, David Cant,*** National Physical Laboratory, UK **INVITED**

'Soft' x-ray based XPS, using aluminium or magnesium anodes, has been a workhorse of surface analysis labs for decades. Over this time, substantial efforts have been made in the development of tools such as sensitivity factors, transmission function corrections, physical parameter databases, simulation software, interpretation methods, and more. Thanks to the existence of such tools, the data obtained from 'soft' XPS, with careful analysis, can provide a strong, quantitative understanding of samples in terms of the relative concentration of elements and their chemistry within the topmost ~10 nm of material. Nevertheless, sometimes 10 nm is not enough.

Until recently, XPS of materials beyond this topmost region of the surface would require either destructive depth profiling of the sample or the use of synchrotron light sources; the former carries its own metrological challenges, as well as ruining a sample, while the latter introduces a plethora of complexities which render calibration difficult. However, recent developments in the design of instruments utilising higher-energy x-ray anodes have begun to make HAXPES instruments more readily available in the lab. This allows far more analysis of samples that previously might have been restricted to synchrotron studies; for example in non-destructive depth-profiling of coated samples with overlayers beyond the ~10 nm limit of 'soft' XPS. Yet with new instruments come new issues; transmission function calibrations that work for the 0 - 1400 eV energy range are not much use for spectra that stretch some KeV beyond, and relative sensitivity factors for each new photon energy and instrument geometry are needed, particularly given the cornucopia of new core levels made available, and the breadth of sensitivity at higher photon energies.

Here we discuss progress towards more quantifiable XPS and HAXPES measurements. A method for the calculation of theoretical sensitivity factors is described, applicable to instruments of any geometry for x-ray sources in the energy range 1.5 - 10 keV, and their validity for depth-profiling of samples well beyond the depths achieved by aluminium sources is demonstrated. We discuss developments in straightforward transmission-function calibrations of standard aluminium sources by the use of a mathematically-defined reference spectrum, as well as progress towards transmission calibration of higher energy sources for which reference spectra do not yet exist. From these developments, the possibility of a 'universal' calibration and sensitivity scheme for both lab- and synchrotron-based HAXPES systems at a range of energies is proposed.

2:20pm **AS+CA+EL+EM+LS+SE+SS-MoA-3 Process-Induced Reactions in Interfaces of High-K/Metal Gate Stacks Studied Using HAXPES*, Thierry Conard*,** *A. Vanleenhove, F. Mascarenhas, I. Hoflijk, I. Vaesen,* IMEC, Belgium

While high-energy photoemission has been in use for decades, it has remained mostly confined to synchrotron radiation facilities. Synchrotron beamlines allow a large flexibility regarding measurement conditions and set-up but are inconvenient in the framework of technological developments, where routine analysis of material systems is needed. The recent availability of performant lab-scale high-energy photoemission spectrometers [1,2,3] alleviate these beamline limitations and thus allow to investigate technological relevant models.

In this presentation, we will demonstrate the potential of HAXPES lab-scale systems regarding application in the semiconductor industry, and more specifically regarding the chemical analysis of interfaces. We will demonstrate the investigation of modifications in layer chemistry of buried layers in multi-layer high-k/metal gate stacks upon thermal treatments. Annealing is one of the critical stages during manufacturing of gate stacks and chemical modification at interfaces play a major role in device performance. With this presentation we will present results on simple stacks such as $TiN/HfO_2/SiO_2/Si$ as well as more complex stacks such as $TaN/TiAl/TiN/HfO_2/SiO_2/Si$ or $W/TiN/HfO_2/SiO_2/Si$. Results will be presented obtained both with Cr Kα (5.4 keV) and Ga Kα (9.25 keV) HAXPES. The respective advantages of these two energies will be discussed in terms of chemical identification, sensitivity and quantification.

Acknowledgement

We are grateful to the Research Foundation Flanders (FWO) for funding the HAXPES Lab instrument within the HERCULES program for Large Research Infrastructure of the Flemish government. Project I014018N.

References

[1]https://www.ulvac-phi.com/en/products/xps/quantes/

[2]https://www.kratos.com/products/axis-supra-xps-surface-analysis-instrument

[3]https://scientaomicron.com/en/system-solutions/electron-spectroscopy/HAXPES-Lab

2:40pm **AS+CA+EL+EM+LS+SE+SS-MoA-4 Quantification and Reporting of XPS Data Taken Under Near Ambient Pressure Conditions – Chances and Challenges in Acquision Speed, Beam Damage, Sensitivity, Reliability, Reproducibility and Repeatability***, P. Dietrich,* ***Andreas Thissen,*** SPECS Surface Nano Analysis GmbH, Germany

Over the last fifty years significant developments have been done in photoelectron spectroscopy instrumentation and thus opened new fields of application. Especially XPS or ESCA developed into a standard analytical method in many labs for surface and material characterization. The number of users and the number of publications using XPS data has tremendously increased. But as a side effect it is a challenge to keep the level of knowledge about the method and correct data interpretation at a high level for all users of these data.

To avoid errors in the interpretation of XPS data instrument manufacturers put efforts inside their instruments and software packages to help and guide the user through data acquisition, data quantification and interpretation and finally also through data reporting. By this data can be made compatible with existing ISO and other community standards. But even more, data quality becomes transparent also in times of open source publications and open data repositories.

For the last ten years XPS under near ambient pressure conditions (NAP-XPS) has gained significant attention in the XPS community. The technique allows for standard analysis of samples under pressures up to about 50 mbar. This opens XPS to liquids, solid-liquid interfaces, gas-solid-interfaces, gas-liquid-interfaces. New fields like operando studies on electrochemical systems, corrosion experiments, analysis of food samples, but also studies of biological samples have been added to the XPS portfolio. The background gas pressure in such experiments is beneficial for the analysis of materials, because it avoids beam damages and degradation due to UHV conditions and also enables true non-destructive analysis of all types of degassing samples and insulators. On the other hand, the absorption of X-rays in the gas atmosphere, the emitted electrons from the gas molecules and inelastic electron scattering in the gas influences the spectral distribution of photoelectrons significantly strongly influencing elemental identification, quantification and detection sensitivity. This presentation summarizes the special challenges in the interpretation of NAP-XPS data and uses several reference samples (mostly published in Surface Science Spectra) from different fields of application. Basic concepts for identification and quantification of spectral features are demonstrated. Finally an outlook is presented how close NAP-XPS is to be a routine metrology technique.

3:00pm **AS+CA+EL+EM+LS+SE+SS-MoA-5 The Modern Spectrometer – Reliable, Repeatable and Relatable***, S. Coultas, J. Counsell,* Kratos Analytical Limited, UK*;* ***Christopher Moffitt,*** Kratos Analytical Inc.*; C. Blomfield,* Kratos Analytical Limited, UK

The outlook of the XPS community has changed significantly in the last decade. The technique has seen constant steady growth due to the rise in surface-based material research – energy storage and harvesting are two such disciplines. This growth of new first-time users needs to be considered, as does the way in which faculties manage centralised analytical facilities. This has led to a change in the philosophy of the workflow of an XPS spectrometer and how the user interacts with the "tool". In this modern era of devolved data and non-expert users the spectrometer itself needs to be reliable, repeatable and relatable. Reliable

– delivers on the promise, Repeatable – consistency with data acquisition and processing, Relatable – simple, easy-to-use, non-expert. This new philosophy creates new challenges for manufacturers who need to deliver the best spectrometer for this new market whilst at the same time maintaining the expectations and beliefs of the traditional analyst.

The discussion will focus on defining the issues of the current XPS outlook and providing practical, workable solutions. The following topics, when combined together, will illustrate the holistic design principles of a modern spectrometer: Simplified workflow, standard methods, automated routines, parameter logging, calibrated and up-to-date sensitivity factors, processing operators, data output and report generation.

3:20pm **AS+CA+EL+EM+LS+SE+SS-MoA-6 Modulation with Atomic Number of the Shirley Background of the Photoemission Spectra of Transition Metals***, **Alberto Herrera-Gomez**, D. Guzman-Bucio,* CINVESTAV-Queretaro, Mexico*; D. Cabrera-German, M. Mayorga-Garay, O. Cortazar-Martinez, J. Torres-Ochoa, A. Carmona-Carmona,* CINVESTAV-Unidad Queretaro, Mexico*; M. Gonzalez Reyna ,* UNAM-Mexico*; V. Crist,* XPS Library*; C. Ospina-Ocampo,* Cinvestav-Unidad Queretaro, Mexico

The 2*p* photoemission spectra of the first-row pure transition metals are similar enough to each other to display a meaningful progression, through the row, of the characteristics of the peaks and background [1]. The same goes for the 3*d* spectra of the second-row pure transition metals [2]. In addition, there are similarities between the behavior of the peak and background parameters of these two rows, such as the dependence of the intensity of the Shirley background with atomic number. The Shirley background is largest for the first column (3B column of the periodic table), decreases to a local minimum to then rise again to a local maximum on the seventh column (8B). The large value of the Shirley background for the first column elements is correlated with the large asymmetry of the main peak and the presence of strong intrinsic plasmons. This correlation might be due to a similar physical origin [3] The local maximum in the 8B column coincides with the maximum of permutations of the valence band, as previously pointed out by Castle and Salvi [4]. The physical mechanism of these phenomena will be discussed.

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4:00pm **AS+CA+EL+EM+LS+SE+SS-MoA-8 Thin Film Analysis by XPS: Quantitative Modeling of Sputtering and Depth Profile Data***, **Lev Gelb**, A. Walker,* University of Texas at Dallas

We present progress in the simutaneous quantitative extraction of both compositional profiles and sputtering parameters from XPS depth-profiles of multilayer films. Depth-profile data are routinely processed to provide “fractional composition vs ion dose” profiles, but such profiles suffer from significant drawbacks: they are constructed assuming that the sample is homogeneous in the probed region, which is not true near interfaces, and it is not normally possible to precisely convert between units of ion dose and depth.

Our approach is to first construct analytical models for both the sample structure and for the erosion process, and then to determine the model parameters (layer thicknesses, interfacial widths, material removal rates, etc.) most consistent with the observed apparent fractional composition profiles. This is done numerically, by comparing simulated and observed apparent composition profiles in a maximum-likelihood framework using an evolutionary optimization algorithm. The only required inputs to the calculation are the “fractional composition” profiles (above) and models for the inelastic mean free paths (IMFPs) for each tracked peak.

We demonstrate the basic idea by analysis of using synthetic data. The resolution of the extracted depth profiles improves when additional peaks are incorporated in the analysis. Small deficiencies in the structure or sputter model do not strongly affect the extracted compositional profiles, while errors in the IMFPs used have much larger effects. We then discuss promising results obtained from the analysis of experimental data from some well-characterized samples. Finally, we discuss improvements and extensions of this modeling/analysis framework. The sputtering model can be extended to include in-sample mixing and chemical reactions. The scheme can also be extended to use complete spectra as input.

4:20pm **AS+CA+EL+EM+LS+SE+SS-MoA-9 Understanding and Controlling Sample Degradation on Modern XPS Spectrometers***, **David Morgan**,* Cardiff University, UK

As XPS systems become ever more user-friendly, with “load-point-click-report” type automated analysis possible, the expertise in understanding samples, their handling and ultimately identifying and dealing with experimental artefacts is slowly eroding.

It has been previously shown that developments in the charge compensation methodology employed, especially the use of dual electron-ion compensation systems, can cause significant damage to a range of inorganic and organic materials [1,2] and in some cases a synergistic effect from the x-rays on the degradation rates can be observed.

Herein, the degradation effect using x-rays and a dual beam neutraliser are explored and discussed, and a delineation of the effects from both neutraliser and the x-rays on a series of polymeric, organic and inorganic materials are presented, together with methodologies to mitigate, or at the very least minimise, such analysis induced damage and propose that which we believe to be a better way of estimating sample damage on a per-system basis than those previously published [3].

[1] L. Edwards, P. Mack and D. J. Morgan, “Recent advances in dual mode charge compensation for XPS analysis”. Surface and Interface Analysis, 51 (2019) 925-933

[2] R. McLaren, G. Owen and D. J. Morgan, “Analysis Induced Reduction of a Polyelectrolyte”, Results in Surfaces and Interfaces, (2021) 100032

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4:40pm **AS+CA+EL+EM+LS+SE+SS-MoA-10 XPS Intensity Calibration and Validation Using Polyethylene and Ionic Liquids***, **Benjamen Reed**,* National Physical Laboratory (NPL), UK*; J. Radnik,* Bundesanstalt für Materialforschung und -prüfung (BAM), Germany*; A. Shard,* National Physical Laboratory (NPL), UK

For quantitative X-ray photoelectron spectroscopy (XPS) analysis, it is necessary to know the *energy-dependent spectrometer response function* ('transmission function') of the XPS instrument. There is a huge variability of transmission functions between different laboratories and instruments, as well as different acquisition parameters for the same instrument. For comparable and reproducible analyses, there is a necessity for a standardised method of intensity calibration and validation.

For intensity calibration, the simplicity of polyethylene’s inelastic background can be described by a mathematical function that can be easily reproduced, is continuous, and noise-free. Instrument geometry must be considered due to the anisotropic emission of photoelectrons and the polarization of monochromated x-rays in many commercial XPS instruments. We therefore present geometry-corrected reference spectra of polyethylene for Al Kα instruments which are traceable to gold, silver, and copper reference spectra from the National Physical Laboratory (NPL). Polyethylene does not require in-situ sample preparation needing only to be scraped with a scalpel before measurement, making it a suitable method for instruments without an ion-sputtering source. VAMAS study A27 determined that over a kinetic energy range of 180 eV to 1500 eV, intensity calibration with polyethylene deviates by ±6.5% compared to previous NPL method using precious metals. Deviations less than 5%, and as low as 1%, are attainable with careful data acquisition from well-maintained instruments. This intensity calibration method is now being developed as an international standard under the auspices of ISO TC201 “Surface Chemical Analysis”.

Once an instrument has been intensity corrected, it is good practice to validate the calibration by measuring a homogeneous sample of known composition. Ionic liquids have several notable properties that make them an ideal material for XPS analysis. Ionic liquids exhibit a high degree of lateral and depth homogeneity, are UHV compatible, and have well-defined stoichiometries. When deposited in recessed sample holder, the meniscus of an IL will be perfectly flat meaning that there are no contributions from sample topographic effects. 1-propyl-3-methyl-imidazolium-bis(trifluoromethyl sulfonyl)imide (Solapur®) is one such IL candidate, with core levels up to ~800 eV binding energy, making it apt for verifying the quantification of light elements, especially for organic materials. Here we present spectra for Solapur® ionic liquid and discuss how they may be used to validate an XPS intensity calibration.

Chemical Analysis and Imaging Interfaces Focus Topic
Room 302 - Session CA+AS+SE+SS-TuM

Progress and Challenges in Industrial Applications

Moderators: Alex Tselev, University of Aveiro, Portugal, **Xiao-Ying Yu**, Oak Ridge National Laboratory, USA

8:00am **CA+AS+SE+SS-TuM-1 Progress on Commercializing Doped Diamond Materials and Devices***, **Anna Zaniewski,*** Advent Diamond **INVITED**

Diamond has long been recognized as a potentially transformative material for power, sensor, and quantum applications. However, realizing the potential of diamond has depended upon a series of breakthroughs in the growth, design, and fabrication of diamond for electronics. Most notably, CVD growth of doped diamond has been a catalyzing breakthrough for realizing next-generation diamond components. Advent Diamond will present progress on achieving commercialization of diamond components and outline future targets for semiconducting and quantum devices.

8:40am **CA+AS+SE+SS-TuM-3 Advanced in Situ Transmission Electron Microscopy: A Powerful Tool for Materials Science, Catalysis, Energy Storage & Lifescience Applications***, **Hugo Pérez-Garza,*** DENSsolutions, Netherlands **INVITED**

We introduce our technology for in situ studies inside transmission electron microscope (TEM), where next to heating and biasing studies, also environmental studies (i.e. in gaseous or liquid environments) are made possible. The systems rely on a Micro Electro-Mechanical System (MEMS)-based device as a smart sample carrier, which contains an integrated set of biasing electrodes or an integrated microheater, to enable in situ electrochemistry, catalytic studies, failure analysis and biomedical studies, among others. As a result, the system provides users with the capability to visualize exciting dynamics in vacuum or liquid/gas environments as a function of different stimuli. In order to provide meaningful results and address historical challenges, our MEMS device controls the flow direction and ensures the gas/liquid will always pass through the region of interest. Thereby, the developed systems offer the opportunity to define the mass transport and control the kinetics of the reaction. Furthermore, the systems allow to control the liquid thickness, enabling resolutions that can go even down to 2.15 Å (for a 100nm liquid thickness). We believe that our developments will play a fundamental role in addressing many of the research questions within battery optimization, fuel cells, (electro)catalysis, as well as for advanced (bio)materials and nanomedicine. Furthermore, it will the unique possibility to visualize biological processes in real time, without the need of vitrifying the biological specimen.

Keywords: Transmission electron microscopy, in situ, MEMS, environmental studies, stimuli

9:20am **CA+AS+SE+SS-TuM-5 Chemical Analysis Using Laboratory-Based Hard X-Ray Photoelectron Spectroscopy: The Binding Energy Reference Challenge***, A. Vanleenhove, F. Mascarenhas, **Thierry Conard,*** IMEC, Belgium

XPS is a well-established technique used for non-destructive analysis of the chemical composition of thin layers and interfaces and is most commonly performed using Al Kα radiation (1486.6 eV), which limits the analysis to the top 5-10nm. The recently developed laboratory-based hard X-ray photoelectron spectroscopes (HAXPES) provide new analysis options. They enable the analysis of thicker film structures and interfaces buried down to 20-50 nm depending on the photon energy and facilitate the analysis of fragile buried layers without ion-induced chemical damage.

This new in-lab technology however comes with new challenges. By the increase of effects which were less pronounced or did not play a role in the analysis with soft X-ray photoelectron spectroscopy the exact binding energy determination and hence analysis of chemical bonding inside layers and at interfaces is more challenging. The recoil effect for instance, which is related to preservation of momentum, resulted in electron energy shifts well within the error bar of peak position determination for XPS spectra. For HAXPES, the recoil effect has to be taken into account, especially when examining low Z materials. Charging effects play a bigger role as well. While charging has to be taken into account for XPS, the analysis of most XPS spectra is quite straightforward as long as the surface charge is stable and the lateral distribution of surface charge is uniform within the area of analysis. For HAXPES however vertical charge distribution comes into the game for a large group of structures whose development can benefit from HAXPES analysis. Vertical charge build up can be complex, especially if examined structures exist of multiple layers and hence multiple interfaces, containing a large variety of materials. But even in ‘simple’ non-conducting one-layer structures a vertical charge gradient builds up when exposed to X-rays and small changes in the parameters of standard surface charge neutralization techniques - as the use of e-beam flood guns - can influence the nature of the charge gradient.

HAXPES spectra of technologically relevant samples will be discussed to demonstrate the challenge of determining exact binding energy values. The set of examined samples comprises complex oxide layers with varying thickness on Si samples and metal/high-k/Si stacks including high-k materials as HfO_2. All experiments are performed in a PHI *Quantes* system and/or a Scienta Omicron *HAXPES Lab*, both equipped with two monochromatic X-ray sources: an Al Kα (1486.6 eV) and a Cr Kα (5414.8 eV - *Quantes*) or Ga Kα (9252.1 eV – *HAXPES lab*) X-ray source.

Acknowledgement

We are grateful to the Research Foundation Flanders (FWO) for funding the *HAXPES Lab* instrument within the HERCULES program for Large Research Infrastructure of the Flemish government. Project I014018N.

11:00am **CA+AS+SE+SS-TuM-10 Integrating Spatial Multiomics Using Giant Cluster Imaging Mass Spectrometry at the Single-Cell Level***, **Hua Tian,*** University of Pittsburgh **INVITED**

Tissue is highly organized with diverse cells that interact and communicate. Together with numerous biomolecules (e.g. metabolites and lipids) of cellular processes, the multilevel heterogeneities drive the biological function and disease-associated discoordination[1-2]. This spatial complexity is often ignored by traditional tissue assay. Mass spectrometry imaging holds the potential to visualize the heterogeneous cell organization and biomolecules in their context. However, it is challenging to achieve high spatial resolution and high chemical sensitivity toward different biomolecules. Moreover, the correlation of spatial omics in a single sample is impossible due to the difficulty of preserving the fast-changing metabolites.

To overcome these analytical hurdles, innovative technology and methodology are developed for omics imaging in single cells. On the same frozen-hydrated tissue, successive $(H_2O)_{n\ (n>28k)}$-GCIB-SIMS and C_{60}-SIMS imaging are employed to profile untargeted metabolites/lipids and targeted proteins by lanthanides antibodies (~ 40 in one acquisition) at 1 µm resolution. The novel ion source, $(H_2O)_{n(n>28k)}$-GCIB enhances chemical sensitivity, improves beam focus, reduces matrix effect, and extends detection ranges up to *m/z* 6000 [3-12]. Coupled with cryogenic analysis, the tissue is analyzed at near nature state, retaining the spatiotemporal distribution of metabolites and lipids. The AI-aided computational processing is used to register the omics in different cell types for further discriminant analysis.

With the new development, a number of tissues are imaged. On breast cancer tissue, the high population of macrophages (CD68) and less infiltration of immune cells (CD45, CD4) are observed, as well as the variation of the metabolic state in different cells. Several phosphatidylinositol species are concentrated in the epithelial tumor cells (pan-cytokeratin), along with desaturated lipids and GSH, indicating the mechanism of immune resistance and antioxidation for tumor survival [27]. Eight ganglioside GM3s correlate with the Ki-67 expressing cells, likely the markers of neoplastic transformation of breast tissue[37]. On liver tissue, distinct lipid clusters colocalize with periportal and pericentral proteins, and metabolic and lipidomic signature varies in distinct liver cells (*e.g.,* sinusoidal, Kupffer, hepatocytes, Ito stellate, immune cells). Similar to protein markers, further clustering analysis shows that metabolites and lipids classify the cell types for the first time. The multimodal SIMS imaging opens broad applications for exploring various biological phenomena of cellular/biomolecular interactions in health/disease.

11:40am **CA+AS+SE+SS-TuM-12 Atom Probe Tomography Using Wavelength-Tunable, Femtosecond-Pulsed Coherent Extreme Ultraviolet Radiation***, **Ann Chiaramonti**, B. Caplins, J. Garcia, L. Miaja-Avila, N. Sanford,* National Institute of Standards and Technology (NIST) **INVITED**

Laser-pulsed atom probe tomography (LAPT) is a powerful tool for materials characterization due to its desirable combination of high spatial resolution and analytical sensitivity. In state-of-the-art LAPT, the thermal pulse resulting from a near-ultraviolet (NUV) laser (E=3.5 eV to 3.6 eV; λ=355 nm to 343 nm) incident on the sample provides the energy to overcome the activation barrier for field ion evaporation.LAPT has been used successfully to characterize a wide range of materials including metals, semiconductors, insulators, biological materials, and even liquids. However, the thermal process is not without drawbacks. LAPT data quality can be degraded due to for example: thermal tails that limit sensitivity; the formation of cluster ions that may have isobaric overlap with elemental species; undetected neutral species which can adversely influence composition measurements; and unresolvable multiple hits which result in a loss of information. Data loss due to multiple hits and neutral species is particularly problematic for many ionic and covalent materials; it can limit the recovery of bulk stoichiometry or composition to a narrow range of experimental conditions, if at all [1,2].

Ionizing radiation in the extreme ultraviolet (EUV) region of the electromagnetic spectrum (E=10 eV to 100 eV; λ=124 nm to 12 nm) offers potential new field ionization pathways (e.g. direct photoionization and Auger decay) for atom probe tomography.Much of the EUV photon energy band is above the work function and ionization potential of any naturally occurring element, and photoionization cross-sections peak in the EUV band across the entire periodic table [3]. EUV is also highly absorbed within only the first few nm of the sample surface.

Instrument design and results from the world’s first EUV radiation-pulsed atom probe microscope are presented. This instrument uses tunable wavelength (photon energy) femtosecond-pulsed coherent EUV radiation from phase-matched high harmonic generation in a hollow waveguide. Initial experiments demonstrate successful EUV (E=41.85 eV; λ=29.6 nm) radiation-pulsed field ion emission in a variety of materials systems. Time-independent background levels, delayed evaporation tails, peak widths, charge state ratios, multiple hit counts, and the relative number of cluster ions will be compared to NUV LAPT experiments on the same samples and specimens.

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Chemical Analysis and Imaging Interfaces Focus Topic
Room 302 - Session CA+2D+AS+BI+HC+LS+NS-TuA

In Situ Microscopy, Spectroscopy and Processing at Liquid-Solid-Gas Interfaces

Moderators: Andrei Kolmakov, National Institute of Standards and Technology (NIST), **Xiao-Ying Yu**, Oak Ridge National Laboratory, USA

2:20pm **CA+2D+AS+BI+HC+LS+NS-TuA-1 Understanding Charge Carrier Variations on the Nanoscale Using Microwave Near-Field Microscopy***, **T. Mitch Wallis**, S. Berweger, P. Kabos,* National Institute of Standards and Technology **INVITED**

Understanding the spatial distributions of charge carriers and their polarity in nanoscale semiconductors and their devices remains a long-standing challenge. Scanning probe-based microwave impedance microscopy (MIM, also called scanning microwave microscopy, SMM) can directly probe charge-carriers on the nanoscale via the high-frequency capacitive interaction between the sharp tip and sample of interest.

Here we will first provide an overview of MIM, including applications to model systems. We will then focus on studies of active devices of semiconducting materials, including GaN nanowires and 2D crystals of elemental tellurium. We will conclude with an overview of recent efforts on photoconductivity mapping in 2D materials and hybrid organic-inorganic lead-halide perovskite thin films. In particular, for the latter we leverage the high bandwidth inherent in the microwave signal to obtain temporal resolution as high as 5 ns.

3:00pm **CA+2D+AS+BI+HC+LS+NS-TuA-3 Oxidation/Reduction of Cu Nanoparticles at a Single-Layer Graphene/Electrolyte Interface Monitored by Scanning Kelvin Probe Microscopy***, **Sidney Cohen**, S. Khatun, M. Andres, I. Pinkas, I. Kaplan-ashiri, O. Brontvein,* Weizmann Institute of Science, Israel*; I. Rosenhek-Goldian,* weizmann Institute of Science, Israel*; R. Weatherup,* Oxford University, UK*; B. Eren,* Weizmann Institute of Science, Israel

The need to probe chemical and physical processes occurring in at liquid/solid interfaces at small scales is being addressed by several cutting-edge techniques. Scanning probe microscopy (SPM) is now a well-established tool for simultaneous morphological, electrical, and mechanical characterization at the nanoscale. Scanning Kelvin Probe microscopy (SKPM) is an SPM method which can measure the work function at nm distance scales. This technique is not conveniently applied within a solution environment. In this work, micro-electrochemical cells were capped by a single layer graphene upper membrane which is transparent to the electrostatic field, enabling high resolution surface measurements of electrical processes occurring at the interfacial liquid region below the membrane. This talk will present this set-up, and show how it can be used to examine stability, and surface interactions in the oxidation/reduction processes of copper nanoparticles (NPs) attached to the graphene under operating (operando) conditions. Complementary techniques including cyclic voltammetry, and ex-situ electron microscopy and x-ray photoelectron spectroscopy gave a complete description of the processes. As an established catalyst for CO_2 reduction, the behavior of Cu in electrochemical conditions is of great interest in both science and technology. The measurements described here provided a nm-scale view of differences in Cu NP oxidation in ambient air and electrochemical conditions, detecting both a galvanic corrosion in air, and reversible reduction of the NPs at cathodic potentials in alkaline solution. Detachment of the NPs after long measurements of redox cycling is documented and rationalized.

3:20pm **CA+2D+AS+BI+HC+LS+NS-TuA-4 Investigation Tritium and Lithium transport along the Tritium-Producing Burnable Absorber Rod***, **Jiyoung Son**,* Pacific Northwest National Lab*; J. Gao,* PNNL*; G. Sevigny, S. Tripathi, B. Matthews,* Pacific Northwest National Lab*; X. Yu,* Oak Ridge National Laboratory

The compositional and microstructural changes in functional materials are critical for nuclear materials in fusion and fission applications. We investigated tritium (^{3}H) and lithium isotope (^{6}Li, ^{7}Li) transport within a neutron-irradiated target rod, aka, Tritium-Producing Burnable Absorber Rod (TPBAR), used in a light water reactor. TPBARs employ the iron aluminide-coated austenitic stainless-steel cladding and associated cruciform as key components. We used multimodal imaging tools and studied the specimens from irradiated TPBAR components. Specifically, a scanning electron microscope with focused ion beam (SEM-FIB) was used to prepare lift-out samples of the irradiated coating and cruciform samples for follow-up microanalysis. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was utilized to detect light isotopes in relation to tritium and lithium diffusion and transport. The observed distributions in the irradiated cladding specimens suggest light isotope mobility between internal target components as a result of neutron irradiation. We compared irradiated claddings of two different configurations in SIMS, and the chemical mapping and depth profiles of aluminide coatings show distinct light isotopic distributions. The cruciform specimens extracted from corresponding locations to the claddings also give interesting results. Overall, advanced correlative imaging results confirm tritium diffusion and lithium transport during the tritium production process. Such results give new insights into the fundamental transport mechanism within the target during irradiation and under non-equilibrium, extreme conditions.

4:20pm **CA+2D+AS+BI+HC+LS+NS-TuA-7 Development of a Workflow for Multiscale Elemental Analysis with X-ray Fluorescence Microscopy and Tomography***, **Si Chen**,* Argonne National Lab*; Y. Luo,* Argonne National Laboratory*; T. Paunesku,* Northwestern University*; O. Antipova, Y. Liu, N. Zaluzec, Z. Di,* Argonne National Laboratory*; G. Woloschak,* Northwestern University **INVITED**

Scanning X-ray fluorescence (XRF) microscopy and tomography provides powerful capabilities to assess the elemental distribution in a three-dimensional (3D) space and differentiate their inter- and intra-cellular interactions in complex biological cells and tissues. Like other microscopy techniques, there is often a tradeoff between spatial resolution and field-of-view that each XRF instrument can provide. For example, XRF nanoprobes are specialized for analysis with <50 nm resolution, but the region can be analyzed within a reasonable time frame is limited to only a few tens of microns. Therefore, the capability to combine the use of multiple instruments becomes important for hierarchical analysis.

In this presentation, we will discuss the Bionanoprobe (BNP) instrument and applications. The BNP is an XRF nanoprobe located at the Advanced Photon Source of Argonne National Laboratory. It is dedicated to the studies of biological tissues and cells with a subcellular spatial resolution. In conjunction with a microscale-resolution XRF instrument, we have demonstrated a workflow to perform multiscale elemental mapping and tomography on HeLa cells treated with non-targeted nanoparticles. While nanoscale tomography revealed the nanoparticle distribution in individual cells, statistical information on cell-nanoparticle interaction was obtained with the microprobe from a large population of cells.

It is important to note the challenges in sample preparation for such multiscale analysis across platforms. Different instruments often require different specimen dimensions in order to achieve their optimal performance. To enable analysis on the same specimen, we have introduced an intermediate specimen manipulation step between micro- and nano-scale measurements utilizing focused ion beam (FIB). Local regions of interest identified with the microprobe were isolated with a FIB instrument and further analyzed at the BNP. Angular enlargement for tomography data collection enabled by the FIB operation significantly improved the tomography reconstruction quality.

5:00pm **CA+2D+AS+BI+HC+LS+NS-TuA-9 in Situ Molecular Imaging of Green Solvents for CO_2 Capture***, **Xiao-Ying Yu**,* Oak Ridge National Laboratory, USA

Switchable ionic liquids are emerging green solvents in for carbon dioxide (CO_2) capture, cleaner separation, and efficient biomass production.However, the liquid structure and composition of SWILs are not fully understood.Besides off-line analyses using NMR and IR, our knowledge of the sustainable green solvents is limited.We used in situ liquid time-of-flight secondary ion mass spectrometry (ToF-SIMS) to study such solvents in this work.This is a unique in situ molecular imaging technique enabled by the invention of a vacuum compatible microfluidic reactor termed system for analysis at the liquid vacuum interface (SALVI).Green solvents of interest were synthesized and reported previously. They were introduced into the microfluidic channel for in situ analysis using liquid ToF-SIMS.Two model systems are illustrated in this talk.The first consists of 1, 8-diazabicycloundec-7-ene (DBU) and 1-hexanol with different CO_2 loadings.The second has koechanol with various CO_2 loadings.Koechanol acts as both acid and base in the latter.Our results show two coexisting liquid phases in these green solvents.This phenomenon was only hypothesized in previous theory prediction.We provide the first physical evidence of the complex liquid – liquid (l – l) interface using three-dimensional chemical mapping with submicrometer resolution.In addition, more complex stoichiometry is discovered due to CO_2 uptake.More importantly, we have provided the first chemical spatial visualization elucidating the evolving l – l interface.The more detailed molecular level understanding of the liquid structure and composition are instrumental to build the foundation for predicative material synthesis, CO_2 capture, and other versatile applications.

5:20pm **CA+2D+AS+BI+HC+LS+NS-TuA-10 Depth Dependence of Salt Ions at the Liquid/Vapor Interface Studied by Ambient Pressure X-Ray Photoelectron Spectroscopy***, A. Siebert, K. Goodman,* ***Monika Blum****,* LBNL

Liquid/vapor interfaces play an important role in chemical, biological, technological, and environmental processes. Perhaps one of the most important interfaces for the environment is the interface between atmospheric aqueous aerosols and the surrounding air, which affects reactions like the scattering and absorption of sunlight as well as the probability of aerosols to serve as cloud condensation nuclei. [1,2] However, the experimental investigation of this active region is complicated by the necessary pressures far away from the ultra-high-vacuum (UHV) region, which is usually required in most surface science studies.[3]

In the recent past, ambient pressure X-ray photoelectron spectroscopy (APXPS) has proven to be a very powerful tool to study the chemical and electronic structure of liquids, solutions, and their interfaces with different media, not requiring the UHV conditions of standard XPS measurements. In this contribution we will utilize a colliding micro flat jet system with synchrotron-based APXPS to gain full insight into the depth dependency of different aqueous salt solutions, e.g. $CaCl_2$,at low salt concentrations. We will present a comparison of bulk ion concentrations in aqueous salt solutions and the surface ion concentration obtained from the ratio between the probed core level area and the peak area of the liquid water phase. This allows us to model the depth profile of salt ions in aqueous solutions and to correlate the data with existing theoretical models.

[1] Havala O. T. Pye et al., Atmos. Chem. Phys., 20, 4809–4888, 2020. [2] Barbara J. Finlayson-Pitts, Phys. Chem. Chem. Phys., 2009, 11, 7760–7779.

Chemical Analysis and Imaging Interfaces Focus Topic
Room Ballroom A - Session CA-TuP

Chemical Analysis and Imaging Interfaces Poster Session

CA-TuP-1 The Metrology Platform for in Operando Characterization of the Diamond Based High Power Devices and Detectors*, Andrei Kolmakov,* NIST

The unique electronic, physical, and thermal properties of diamond make diamond-based devices one of the most prospective for high-power electronics and detectors. The doping of diamond, however, appears to be a challenge due to high activation energy of the common p- or n-dopants. Alternative p-type doping via diamond surface hydrogenation is a key process to fabricate modern high mobility FETs.

Here we report on a simple design of the remote plasma reactor for gentle diamond surface hydrogenation. To avoid the uncontrolled surface adsorption of acceptor-like adsorbates and related band bending the design of the reactor is made as a vacuum suitcase to transfer the as-prepared device between different characterization facilities. We demonstrate the lithographic procedures and performance of the corresponding devices via measuring the properties of the electron detector and high mobility FET devices.

CA-TuP-2 Using Complimentary Characterization Techniques to Understand Interfacial Phenomena*, Vincent Smentkowski,* GE-R*; I. Spinelli, M. Knussman, M. Larson, J. Della Villa,* 1 Research Circle

Coatings and films are frequently applied to (or form on) substrate materials for a variety of reasons.Robustness of the coating is often dependent on the microstructure and/or cleanliness of the substate prior to deposition of the coating.In this presentation, we will show that the best understanding of the interfacial chemistry is obtained when multiple, complimentary, characterization techniques are used; namely scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), time of flight secondary ion mass spectroscopy (ToF-SIMS), metallography, and focused ion beam (FIB).The benefits of 3D analysis will be highlighted.We will also address the limitations associated with each of the techniques.

Applied Surface Science Division
Room 320 - Session AS+BI+CA+HC+LS+PS+SE+SS-WeM

Analysis of Surfaces and Interfaces Related to Energy and the Environment

Moderators: Kateryna Artyushkova, Physical Electronics, **Tony Ohlhausen**, Sandia National Laboratory

8:00am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-1 Adhesion Properties of Industrial Steel Samples***, **Lukas Kalchgruber**, M. Hahn, L. Mears, M. Valtiner,* TU Wien, Austria

Solving industrial questions is of utmost importance to improve material properties, developing industrial applications and understanding fundamental processes. One of these questions is how different pre-treatments alter the adhesion process between steel and polymers.

To study the effect of the pre-treatment on the subsequent adhesion process, steel was treated either thermally or via plasma.

To characterize adhesion, the surface force apparatus (= SFA) was utilized in reflection mode. In the SFA experiment, the steel is brought into contact with another surface which is prepared on a fused silica optical disc. Before the optical discs can be used in SFA, a semitransparent, reflective layer needs to be deposited on the curved surface. Additionally, they were spin coated with few µm thin, homogeneous, smooth layers of SEBS polymer. Afterwards, a suitable particle free contact was established between the polymer and the steel sample in the SFA, which generated the following data types:

1. Newton rings à Provide information about the contact area
2. Force data à Adhesive pressure (referenced to contact area)
3. Fringes of chromatic order (= FECO) à Time-Distance-Curves

The main selling points of this technique are as follows: firstly, the model system is very close to the actual problem, as the steel sample in question can be used directly. Secondly, direct information about the adhesive pressure can be obtained. Thirdly, considerably more information about the adhesive behavior of the system is available beyond just one number.

The SFA results achieved are promising. We have a method that allows us to quantify the adhesive pressure in a model system and differentiate between differently treated steel samples. We have further put our adhesion results into context with the support of XPS characterization of the surface. Thermally treated samples have a hydroxide/oxide ratio of roughly 50/50 while samples treated with plasma show a ratio of 90/10. The hydroxide to oxide ratio correlates with the adhesion measured by SFA, which emphasizes the role of hydroxide in preventing adhesion.

8:20am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-2 An Electrochemically Polymerized Protective Layer for Magnesium Metal Anode***, Y. Wang,* University of Maryland College Park*; **Alexander Kozen,*** University of Maryland

Rechargeable magnesium (Mg) batteries are promising beyond Li-ion technologies due to their high volumetric capacity (3832 mAh cm^{-3}) and high natural abundance. Nonetheless, Mg metal anode is incompatible with most conventional electrolytes which leads to the formation of an ionically passivating layer. Mg also suffers from growth of dendrites similar to Li, which causes failure of the cells. In this study, we electrochemically polymerized 1,3-dioxolane (DOL) to form a thin Mg^{2+}-conducting elastomeric artificial solid electrolyte interphase (ASEI) layer by electrochemically pretreating Mg metal anodes. We found that this protective ASEI layer enables excellent cyclability of Mg-Mg symmetric cells at high current density (0.5 $mAcm^{-2}$) over 400 hours at a stable low overpotential (0.50 V vs. Mg^{2+}/Mg) without cell short-circuiting, while untreated pristine Mg symmetric cells quickly failed. The formation of this ASEI also significantly lowered the impedance of the cells, which proved its capability of conducting Mg^{2+} ions. Comprehensive surface chemistry analysis was done by X-ray photoelectron spectroscopy (XPS) which showed that an ASEI mainly consists of poly-DOL was formed, along with various Mg salts which are instrumental to the conductance of Mg^{2+} ions. More importantly, poly-DOL component in the elastomer was well preserved post-cycling, which contributed to the long-term cyclability and low voltage hysteresis of pretreated Mg-Mg cells, as compared to the pristine ones. Focused ion beam (FIB) – scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) mapping showed that a generally uniform layer was formed on the surface and this ASEI is roughly 200 µm thick and was able to suppress the growth of Mg dendrites after cycling for 400 hours at 0.03 mA cm^{-2} current density, as compared to the rampant sphere-shaped dendrites on the surface of pristine Mg anodes after cycling. This is the first ever report on the successful formation of poly-DOL ASEI on Mg metal anodes as a protective layer and by electrochemical polymerization method that effectively enhanced the electrochemical cycling performance of the Mg metal anodes.

8:40am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-3 Analysis of Surfaces and Interfaces in Polymer Electrolyte Membrane Fuel Cell and Electrolyzer Devices***, **Svitlana Pylypenko**,* Colorado School of Mines **INVITED**

Implementing a hydrogen-based infrastructure depends on developing electrochemical energy conversion devices such as fuel cells and electrolyzers. Polymer electrolyte membrane fuel cells (PEMFCs) have been the focus of research for lightweight renewable transportation applications such as motor vehicles for years, but they also offer the potential to fuel stationary applications, including residential power, due to their potential to produce industrial amounts of energy via a renewable route. Polymer electrolyte membrane water electrolysis (PEMWE) is a promising strategy to produce and store renewable energy in the form of hydrogen for subsequent use in either manufacturing processes, or to run a fuel cell, which can generate electricity on demand.

Great improvements have been made in the development of catalysts and electrodes for PEM systems, improving their activity and stability while reducing the amount of precious metals used. The properties of the electrodes used in these devices are influenced by multiple parameters: the chemical identity of the catalyst and the ionomer; the morphological properties of the catalyst (e.g. shape and surface area); ink formulations; and the various processing parameters used to prepare the electrode. Due to the breadth of possible variable combinations and the inherent complexity of electrode materials, it is unsurprising that PEM electrodes are both morphologically and chemically heterogeneous. Characterization of relevant surfaces and interfaces in these devices, therefore, represents a challenge that requires a multi-technique approach that evaluates all relevant scales and properties and brings a better understanding of the evolution of surfaces and interfaces under more realistic conditions. This talk will discuss the progress towards the comprehensive characterization of the most critical surfaces and interfaces in PEM devices using a combination of X-ray and electron spectroscopy and microscopy methods. Several challenges related to the characterization of catalyst-gas and catalyst-ionomer interactions in these systems will be covered along with results obtained with near-ambient pressure x-ray photoelectron spectroscopy (nAP-XPS). The development of characterization strategies to enable the exploration of a large processing parameter space will be presented, which can then be used to fabricate optimized electrodes with state-of-the-art catalysts as well as electrodes that integrate novel catalysts, all made with scalable routes. And finally, the development of novel approaches toward the characterization of other components of PEM devices such as porous transport layers will also be briefly discussed.

9:20am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-5 XPS Analysis of Battery Materials***, **Sarah Zaccarine**, B. Schmidt, K. Artyushkova,* Physical Electronics USA*; A. Baniya, Q. Qiao,* Syracuse University

Lithium-ion batteries (LIBs) have experienced success including rechargeability and long lifetimes but their limited energy density restricts applications moving forward. Lithium metal batteries (LMBs) offer similar benefits but with much higher achievable energy densities, making them a promising future battery technology. Both LIBs and LMBs are multi-layered, complex systems with many materials and interfaces that each play a critical role in performance and stability. Tuning the composition and morphology of these materials is necessary to create stable, high-performing devices, but the multi-component interfaces, interactions, and dynamic nature of these systems makes characterization challenging. In order to optimize materials properties and improve battery lifetimes, there is a pressing need for physicochemical characterization approaches with high spatial resolution, chemical and morphological analysis, and correlation of synergistic properties.

X-ray photoelectron spectroscopy (XPS) is commonly used to characterize the chemical composition of battery materials, and the depth resolution (~10nm) is ideal for analyzing thin layers and interfaces. However, modern XPS instruments have a variety of operating modes and analytical accessories that enable characterization across a variety of lateral and vertical size regimes. Small and large spot comparisons can track overall composition and local features and changes, with scanning microprobe analysis allowing for spatial resolution down to a few microns. X-ray induced secondary electron imaging (SXI), including high-resolution mosaic imaging over a wide sample area, can be used for easy identification of important features and morphological imaging of various battery component materials to complement chemical information. Chemical mapping can visualize distribution of individual elements or chemical species to understand how materials are distributed and change with testing. Additional options address stability concerns associated with Li materials, including a cooling stage to preserve battery chemistry during extended experiment times, where time-resolved profiles are used to compare chemical degradation under controlled temperatures, and incorporating Al Kα and Cr Kα X-rays for non-destructive XPS and hard X-ray photoelectron spectroscopy (HAXPES) analysis of surface (up to ~10nm, Al) and subsurface (up to ~30nm, Cr) composition. Combined, these powerful capabilities enable thorough characterization of battery materials properties for micro- and large-area spectroscopic analysis of surfaces and interfaces and how these properties change under various analytical and operating conditions.

9:40am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-6 Novel Battery Material Analysis with High-Resolution and High-Throughput XPS***, J. Counsell, S. Coultas,* Kratos Analytical Inc., UK*; C. Moffitt,* Kratos Analytical Inc.*; C. Blomfield,* Kratos Analytical Inc., UK*; **Adam Roberts**,* Kratos Analytical Limited, UK

Several material systems will be discussed to give an overview on how XPS can yield information regarding the distribution and chemical speciation of battery materials.

Na-ion batteries are considered to be environmentally favourable alternatives to Li-ion batteries, particularly in the extremely large-scale application of grid storage, given the abundance of Na. However, to date, the battery performance has not been competitive, and promising ternary materials have been plagued by poor stability in air and unsatisfactory long-term cycling. Herein, air/moisture stability is effectively and systematically investigated with XPS, paving the way for material stability to be modified through rational design. Chemical assignments were correlated with performance and oxidation degradation [1]

The significance of sensitivity and detection limit, comparisons of surface and bulk and an approach for pragmatic peak fitting of difficult elemental lines will be discussed along with considerations such as etch artefacts and degradation.

[1] Shipeng Jia *et al*., J. Mater. Chem. A, 2022,10, 251-265

11:00am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-10 Multimodal Analysis and Imaging of the Boehmite Layer on AA6061***, **Lyndi Strange**,* Pacific Northwest National Lab*; X. Yu,* Oak Ridge National Laboratory*; V. Shutthahandan, M. Song, Q. Miller, M. Bowden, J. Gao, Y. Zhang, J. Son, R. Shimskey, R. Prabhakaran,* Pacific Northwest National Lab*; V. Joshi,* Pacific Northwest National Laboratory

Low-enriched uranium (LEU) alloyed with 10% Mo (U-10Mo) is being considered as a promising alternative to oxide-based dispersion fuel with high-enriched uranium for use in research reactors. The configuration of this proposed LEU monolithic fuel plate consists of the U-10Mo plate-type fuel foil with a 25 µm Zr interlayer barrier clad with an aluminum alloy (AA6061). The clad AA6061 is coated with a boehmite layer to prevent corrosion. The boehmite layer has a high pH passivation range, which makes it resistant to oxidation and preferable to protect the Al cladding. Boehmite is usually formed on the AA6061 surface by autoclave processing. Various surface cleaning techniques have been employed such as polishing and etching to clean the surface of the AA6061 prior to boehmite formation. In this study, we examine how pre-treatment of AA6061 using polishing followed by both acid and alkaline etching affects the chemical composition of the boehmite layer using multimodal analysis. Time-of-flight secondary ion mass spectrometry (ToF-SIMS), x-ray photoelectron microscopy (XPS), transmission electron microscopy (TEM), and grazing incidence x-ray diffraction (GI-XRD) were used to understand the changes in the boehmite layer as a result pre-treatment. ToF-SIMS provides a surface sensitive technique to understand the surface composition and characteristics. Spectral similarities were verified using principal comment analysis (PCA). XPS is a complimentary technique that provides quantitative information about the oxidation states present on the surface. Both the SIMS and XPS results suggested oxidation at the surface, which was further investigated using TEM-SAED and GI-XRD. While the GI-XRD results suggested the dominant phase present on the coupon surface is boehmite, TEM-SAED found small amounts of α- and γ-Al_2O_3 present as a result of alkaline etching.

11:20am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-11 Study of $Cs_x(CH_3NH_3)_{1-x}PbBr_3$ Perovskite with XPS Imaging and Small Area Spectra***, **Tatyana Bendikov**,* Weizmann Institute of Science, Israel*; Y. Rakita,* Columbia University*; H. Kaslasi, G. Hodes, D. Cahen,* Weizmann Institute of Science, Israel

Interest in halide perovskite (HaPs) is motivated by the combination of superior optoelectronic properties and ease in synthesizing these materials with a surprisingly low density of electrically active defects.[1] HaPs possess high chemical sensitivity, especially those having an organic cation at their *A* position (AMX_3). Although a direct role of the *A* cation in this sensitivity is unclear, and the structural and optoelectronic backbone lie within the *M-X* bond, the type of the *A* cation was shown to impact the chemical stability and, usually indirectly, affect optoelectronic properties of HaPs.[2-3]

X-ray Photoelectron Spectroscopy (XPS), is a surface sensitive technique with a sensitivity that goes down to a single atomic layer, and can provide unique information that relates the elemental composition with the chemical and electronic states of the different elements in the material. Our study focuses on the XPS imaging in combination with selected small area XPS spectra and uses solution-grown, single crystals of mixed *A*-cation $Cs_xMA_{1-x}PbBr_3$(MA = $CH_3NH_3^+$) HaPs as a candidate for investigating heterogeneity within the crystals. With XPS we followed the variations in chemical composition of these crystals. By observing the surface, we found significant changes in the N/Cs ratio, which increases towards the interior of the crystal. Similar variations in N/Cs, but also in Pb/(N+Cs) ratios were found when we studied cross-sections of cleaved crystals. This compositional heterogeneity within the HaPs crystal was not previously reported and was discovered and monitored due to exclusive capabilities of the XPS technique.

References:

1. P. K. Nayak, S. Mahesh, H. J. Snaith, D. Cahen, *Nat. Rev. Mater*., **2019**, *4*, 269-285.
2. H. Kaslasi, Y. Feldman, Y. Rakita, D. Cahen, G. Hodes,*Cryst. Growth Des*, **2020**, *20*, 4366-4374.
3. D. R. Ceratti, A. V. Cohen, R. Tenne, Y. Rakita, L. Snarski, N. P. Jasti, L. Cremonesi, R. Cohen, M. Weitman, I. Rosenhek-Goldian, I. Kaplan-Ashiri, T. Bendikov, V. Kalchenko, M. Elbaum, M. A. C. Potenza, L. Kronik, G. Hodes, D. Cahen, *Mater. Horiz.*, **2021**, *8*,1570-1586.

11:40am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-12 Surface Characterization of Mineral Associated Organic Matters in Environmental Samples by Using X-Ray Photoelectron Spectroscopy (XPS)***, **Qian Zhao**, M. Engelhard, O. Qafoku, K. Hofmockel,* Pacific Northwest National Laboratory

Surface characterization is an important analytical approach to understanding the most dynamic interface of a material. The understanding of soil organic matter (SOM) persistence is critical to global carbon (C) cycling. Minerals play an important role in persisting SOM by associating with organic matters (OM) through different interactions. Yet mechanisms of the accumulation of OM in soil are still unclear. Chemical characterization of OM that is associated with minerals provides a mechanistic understanding of mineral-OM interactions. X-ray photoelectron spectroscopy (XPS) analysis allows us to probe the chemical states and speciation of OM on the surface of mineral grains or soil 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 adsorbed four organic compounds on a calcite crystal. XPS analysis found the relative concentration of C was higher in OM adsorbed calcite than that in pristine calcite. Further, the deconvolution of C 1s spectra reveals that the calcite surface had a relatively lower abundance of carbonate but a higher abundance of alkanes in the OM adsorbed calcite than pristine calcite, indicating the adsorption of OM on the calcite surface. In the soil system, we incubated agricultural soils with ^{13}C-glucose for 12 months to trace the fate of microbial residues. Size and density fractionation was used to separate mineral-associated organic matter (MAOM) from whole soil. XPS analysis determined C chemistry of necromass on soil particle surfaces by scanning C 1s region of MAOM and non-MAOM fractions. We found that the MAOM fraction had a relatively higher abundance of carbonyl and carboxylic C functional groups and a relatively lower abundance of C-C/C=C group than non-MAOM fraction. It suggests that MAOM fraction is enriched in microbial-derived molecules (i.e., proteins) but has fewer plant detritus (i.e., carbohydrates or lignin) on mineral surfaces. XPS technique allows us to understand the surface chemistry of microbial necromass that is associated with minerals in soil. The chemical speciation information provides us with the potential bonding environment at the interface of minerals and OM.

Chemical Analysis and Imaging Interfaces Focus Topic
Room 302 - Session CA+HC+LS+VT-WeM

Multiphase Interfacial Analysis and Imaging

Moderators: Andrei Kolmakov, National Institute of Standards and Technology (NIST), **Slavomir Nemsak**, Advanced Light Source, Lawrence Berkeley National Laboratory

8:00am **CA+HC+LS+VT-WeM-1 Probing the Impact of Nanoscale Defect Sites in Perovskite Photovoltaic Films with Time-Resolved Photoemission Electron Microscopy***, **Keshav Dani**,* 1919-1 Tancha, Kunigami-kun, Japan **INVITED**

Hybrid perovskite photovoltaic devices have rapidly emerged as promising contenders for next generation, low-cost solar cell technology. Yet, the presence of defect states critically impacts device operation, including device efficiency and potentially long-term stability. Understanding the nature of these defects, and their role in photocarrier trapping, requires techniques that are capable of probing ultrafast photocarrier dynamics at the nanoscale.

In this talk, I will discuss the development of time-resolved photoemission electron microscopy (TR PEEM) techniques in my lab [1, 2], applied to hybrid perovskite solar materials. Thereby, we directly visualize the presence of the performance limiting nanoscale defect clusters and elucidate the role of diffusion in the charge carrier trapping process [3]. By correlating PEEM measurements with other spatially resolved microscopies, we identify different types of defects that form, and study how passivation strategies may have a varied impact on them [4]. Finally, we show that these defect can act as seeds for degradation [5].

[1] M. K. L. Man, *et al.* Imaging the motion of electrons across semiconductor heterojunctions. *Nature Nanotech.***12**, 36 (2017).

[2] E. L. Wong, *et al.* Pulling apart photoexcited electrons by photoinducing an in-place surface electric field. *Science Advances***4**, eaat9722 (2018).

[3] T. A. S. Doherty*, A. J. Winchester*, et al.Performance-limiting trap clusters at grin junction in halide perovskites. *Nature***580**, 360 (2020). *equal authors

[4] S. Kosar, et al. Unraveling the varied nature and roles of defects in hybrid halide perovskites with time-resolved photoemission electron microscopy. *Energy Environ Sci*. 14, 6320 (2021)

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8:40am **CA+HC+LS+VT-WeM-3 Correlating Structure and Chemistry Using Ambient Pressure Photoemission and X-Ray Scattering***, **Slavomir Nemsak**,* Lawrence Berkeley Laboratory Advanced Light Source **INVITED**

In the last two decades, Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) has established itself as a go-to technique to study heterogeneous and complex materials under reaction environments. Multimodal approaches, which correlate information from two or more complementary techniques, are currently one of the forefronts of the APXPS development [1]. In the past three years, the ALS contributed one such setup: a combined Ambient Pressure PhotoEmission and X-ray Scattering (APPEXS) instrument commissioned and operated at beamline 11.0.2 [2]. The combination of the two in-situ techniques allows correlating structural and chemical information. By using APPEXS, we observed dynamics of the exsolution process of catalyst metallic nanoparticles [3]. To expand the capabilities of APPEXS further, we introduced a new platform using arrays of patterned nanoparticles to study the evolution of catalytic systems under reaction conditions [4]. Future developments of the technique(s) will be also discussed.

References

[1] H. Kersell et al., Ambient Pressure Spectroscopy in Complex Chemical Environments, 333-358 (2021).

[2] H. Kersell et al., Rev. Sci. Instr. 92, 044102 (2021).

[3] H. Kersell et al., Faraday Discussions, accepted (2022).

[4] H. Kersell et al., Synchr. Rad. News, accepted (2022).

9:20am **CA+HC+LS+VT-WeM-5 Gating of the 2D Hole Transport in Diamond by Subsurface Charges***, E. Strelcov, **Andrei Kolmakov**,* NIST

The unique electronic, physical, and thermal properties of diamond make diamond-based FETs one of the most prospective devices for high-frequency power electronics. Transfer doping of hydrogenated diamond is a common process to form 2D conducting channels in diamond FET. The electron /hole transport of such a device is sensitively dependent on near-surface scatters including charged traps.

Here, using SEM (EBIC) and AFM Kelvin probe force (KPFM) microscopies we report on imaging of the hole transport in narrow conducting channels as a function of the density and depth of near-surface charges. We demonstrate the gating effect induced by trapped charges and discuss the methods to minimize these effects.

9:40am **CA+HC+LS+VT-WeM-6 Development of 0–D Argon Collisional Radiative Model conjoined with Optical Emission Spectroscopy between 1 mTorr to 760 Torr***, **Tag Choi**, N. Abuyazid, D. Patel,* University of Illinois at Urbana-Champaign*; D. Jacobson,* LytEn. Inc*; S. Keniley, S. Dubowsky, D. Barlaz, D. Curreli, D. Ruzic,* University of Illinois at Urbana-Champaign

Optical emission spectroscopy (OES) is a non-invasive plasma diagnostic, which can be utilized with 0-dimensional argon collisional radiative model (Ar CRM) to understand dynamics of excited and charged argon species and determine plasma parameters in the system. This work aims to study rate coefficients of excited and charged argon species, calculate their densities over time and verify the theoretical results with experimental optical spectra in a wide range of pressure regimes. The model considers various types of collisions such as electron and atom excitation/ionization, photon emission, diffusion, penning ionization, and excimer formation. A merit function is used to obtain a better correlation between the theoretical and experimental densities of the various argon species. This allows the model to get a more accurate estimate of the electron temperature and the densities. Various plasma sources are used such as a low pressure inductively coupled plasma (ICP) source, dielectric barrier discharge (DBD), and microwave discharges, to produce different types of plasmas at pressure ranges of 10 – 50 mTorr and 1 – 760 Torr. The optical emission spectra and Langmuir probe measurements are collected for verifications on a low pressure ICP source and DBD discharge. For the verification of atmospheric microwave discharge, OES data is collected for temperature calculations from Specair and the model. Different plasma sources produce different electron temperatures and densities. The ICP source, DBD and microwave discharge have electron temperatures (T_e) of 2 – 5 eV, 1 – 3 eV, and 0.4 – 0.6 eV and electron density (n_e) of 1E16 to 1E18 m^3, 1E18 to 1E21 m^3, and 1E19 to 1E22 m^3 respectively. A methane and argon gas mixture are introduced to the microwave discharge to understand how plasma parameters differ from a pure argon environment.

11:00am **CA+HC+LS+VT-WeM-10 Atomic-Scale Modeling of Bismuth and Argon Clusters Sputtering of Water/Vacuum Interfaces***, **Zbigniew Postawa**, M. Kański, C. Chang, S. Hrabar,* Jagiellonian University, Poland **INVITED**

Modeling of water/vacuum interfaces should consider the high vacuum pressure of water. First, there is continuous evaporation of the liquid into the vacuum chamber, which must be considered. This phenomenon poses a significant challenge for conventional experimental techniques. Yang *et al.* presented a way to reduce the impact of this phenomenon by using a microfluidic channel [1]. This approach uses an ion beam to drill a 2-3 µm window in the channel wall, exposing the liquid flowing below. Such an arrangement allows for maintaining a low base pressure (~10^{-7} mbar) in the measuring chamber. This technique has already been used to study photochemical reactions, biofilms, and liquid-liquid interfaces by secondary ion mass spectrometry or secondary electron microscopy [2]. Recently, another approach minimizing the effect of high vacuum pressure of water that uses a graphene cell encapsulating a liquid was proposed in studies with transmission electron microscopy [3].

Recently, we have developed a new ReaxFF potential parameterization for modeling C/H/O systems designed directly for sputtering simulations [4]. This parametrization is up to 3 times faster than standard ReaxFF. New force-field allowed us to perform molecular dynamics computer simulations of water and graphene-covered water systems sputtered by bismuth and argon clusters. The mechanism of molecular emission from these two systems is investigated. The effect of the projectile size and the influence of the protecting graphene sheet on the emission process is discussed.

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Acknowledgments

The work has been supported by Polish National Science Center Grant 2019/33/B/ST4/01778 and the PLGrid Infrastructure.

11:40am **CA+HC+LS+VT-WeM-12 Finite-Elements Modeling of Solid-Electrolyte Interfaces in Through-Membranes Imaging and in-Liquid Scanning Probe Experiments***, **Alexander Tselev**,* Department of Physics & CICECO-Aveiro Institute of Materials, University of Aveiro, Portugal **INVITED**

Studies of the physicochemical processes at the interfaces between solids and electrolytes interfaces require *operando* multi-parametric measurements with chemical and electric potential sensitivity, in-depth selectivity, as well as with a high lateral resolution. A number of experimental techniques were implemented for this purpose. In this talk, we will describe applications of finite-elements (FE) modeling to elucidate and interpret microscopic imaging and measurements with liquids ranging from non-polar ones to decimole electrolyte solutions. This includes probing through graphene membranes with the use of microscopy and spectroscopy tools based on high-energy beams—X-rays and electron beams, as well as low-energy probing with the use of scanning probe techniques. Scanning probe techniques can be implemented both with probes in liquids and with probes separated from the electrolytes by membranes. We will discuss liquid-solid interface probing by the Kelvin probe force microscopy (KPFM) through graphene membranes as well as by near-field microwave microscopy through dielectric membranes. Furthermore, models for piezoresponse force microscopy and KPFM with probes immersed in electrolytes will be presented. Support of this work by the project CICECO-Aveiro Institute of Materials, financed by national funds through the FCT/MEC (Portugal) and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement is acknowledged.

Applied Surface Science Division
Room 320 - Session AS+CA+HC+LS-WeA

Shining a Light on Surface Chemical Metrology: In Memory of Martin Seah

Moderators: Donald Baer, Pacific Northwest National Laboratory, **Alexander Shard**, National Physical Laboratory, UK

2:20pm **AS+CA+HC+LS-WeA-1 Metrology Lights the Way for Advances in Metabolic Imaging at the Single-cell Scale*, Ian Gilmore,*** National Physical Laboratory, UK **INVITED**

The international community recently paid homage to Martin Seah in a Special Issue of Surface Interface Analysis [1] with reminiscences, biographical accounts of his considerable achievements, reviews and research articles. The collection takes its title “Shining a light on surface chemical analysis” from Martin’s research career of over 5 decades dedicated to guiding the community to make better measurements in traditional and emerging areas of surface chemical analysis. Where there was darkness, he brought light. Here, we begin with a retrospective look at Martin’s considerable achievements in XPS, AES, SIMS, AFM and leadership in International Standardisation.

Martin was never one for too much retrospection though and was always full of energy and enthusiasm to tackle the issues of tomorrow. We therefore show how by using Martin’s methodology that metrology is lighting the way for metabolic imaging at the single-cell scale, which is of critical importance in the development of new pharmaceuticals, understanding tumour heterogeneity and fundamental biological studies to understand metabolic rewiring in diseases.

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3:00pm **AS+CA+HC+LS-WeA-3 Two-Point Calibration Method for Quantifying Organic Binary Mixtures Using SIMS in the Presence of Matrix Effects*, Alexander Shard,*** National Physical Laboratory, U.K.*; A. Miisho,* Kobelco, Japan*; J. Vorng, R. Havelund, I. Gilmore,* National Physical Laboratory, U.K.*; S. Aoyagi,* Seikei University, Japan

Quantification of composition for organic mixtures is required in the analyses of technological materials from organic electronics to drug delivery systems. The molecular specificity of secondary ion mass spectrometry provides an unparalleled ability to distinguish organic materials, however it is difficult to use for quantitative analysis. In a few cases, there is a linear dependence between the composition, expressed as a ratio of component volumes, and the secondary ion intensities, expressed as a ratio of intensities of ions from each component. However, this ideal relationship fails in the presence of matrix effects and linearity is observed only over small compositional ranges, particularly in the dilute limits. We present an empirical method which introduces a power law dependence between the intensity ratio and the volume fraction ratio. A physical model of the organic matrix effect is employed to test the limits of the method and a mixed system of 3,3’-bis(9-carbazolyl) biphenyl and tris(2-phenylpyridinato)iridium(III) is used to demonstrate the method. In practice, we describe a two-point calibration, which determines both the exponent in the power law and the sensitivity factor for the conversion of ion intensity ratio into volume fraction ratio. We demonstrate that the two-point method significantly improves the accuracy of quantification compared to a one-point, linear calibration and is valid over a wide compositional range. Since the method enables the use of clearly identifiable secondary ions for quantitative purposes and mitigates commonly observed matrix effects in organic materials, the two-point calibration method could be of significant benefit to SIMS analysts.

3:20pm **AS+CA+HC+LS-WeA-4 OrbiSIMS Metrology: Optimization of Inorganic Depth Profiling using Ge and Sb Delta-layer Samples***, Y. Zhou,* National Physical Laboratory, UK*; A. Franquet, V. Spampinato,* IMEC, Belgium*; A. Pirkl,* IONTOF GmbH, Germany*; W. Vandervorst, P. Van Der Heide,* IMEC, Belgium*; **Ian Gilmore,*** National Physical Laboratory, UK

In 2017, NPL introduced the 3D OrbiSIMS instrument [1] for sub-cellular resolution molecular imaging with high-mass resolution and mass accuracy (> 240,000 at m/z 200 and < 2 ppm, respectively). Since then, IONTOF installed multiple Hybrid SIMS systems around the world with a growing range of applications, largely in, but not limited to, the life-sciences.[2,3] The dual ToF-MS and Orbitrap-MS analyzers combined with Bi liquid metal, gas cluster, and low energy $O_2^+$and Cs^+ ion beams provide a highly versatile platform for materials science studies.

Since the Orbitrap-MS is designed to operate with a continuous ion source, the instrument is well configured to take advantage of single ion beam depth profiling approaches. For example, Sul et al[4] recently demonstrated the ability to sputter depth profile a blue phosphorescent OLED device using GCIB sputtering with Orbitrap-MS. Similarly, Spampinato used the high-mass resolving power of the Orbitrap-MS to study thin EUV photoresist films where ToF-SIMS suffered from severe molecular interferences. [5] Moreover, there is growing interest in the application of the OrbiSIMS to inorganic semiconductors. Franquet et al[6] recently showed how the high mass resolution of the Orbitrap-MS analyzer combined with 2 keV Cs^+ sputtering enabled the composition of SiGe architectures down to < 20 nm to be determined with improved accuracy using the Self Focusing SIMS methodology.[6]

In this study, we use a sample consisting of 8 Ge delta-layers with a spacing of 4.8 nm in a silicon matrix. The thickness of each delta-layer is ~0.2 nm with a concentration of below 1 atom%. A second sample consisting of 5 Sb delta-layers with a spacing of 10 nm in a silicon matrix was also used. A sputter gun using either O_2^+or Cs^+ between 1 keV and 2 keV was used for both sputtering and analysis with Orbitrap-MS detection. The optimization of instrument parameters including sputter rate, injection time and sputter beam energy on the depth resolution (λ_g, λ_d and Gaussian broadening)[7]will be discussed.

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4:20pm **AS+CA+HC+LS-WeA-7 Complementary Perspectives on the Impacts of Martin Seah on Surface Analysis*, Don Baer,*** Pacific Northwest National Laboratory **INVITED**

Throughout his more than four decade career Dr. Martin Seah had a major impact on quantitative surface analysis and the surface analysis community. There were many facets to his activities, interactions, and leadership and most of those who interacted with him knew only a portion of his many contributions. This talk will describe ways that he impacted my career and some of the activities that may have been less visible to many in the surface analysis community. Accurate quantitative surface analysis was a theme throughout his career. My introduction to his work was associated with measurements of the segregation of trace elements to the grain boundaries of metals and metal alloys.In the 1970s understanding of the challenges to quantitative analysis of electron spectroscopy was evolving and results were often inconsistent and sometimes a source controversy. Work by Seah and Hondros was important to put these measurements on a sound foundation. An important trait of Martin’s work was his ability to identify needs or information gaps and to proceed to fill them.There are many examples of this, including application of XPS to measure very thin oxide films on silicon wafers, simple models of electron mean free path lengths, models for understanding sputtering rates of cluster ion sources and the development of consistent terminology for surface methods and analysis. Martin made significant and enjoyable efforts to communicate information to the community and offered encouragement to other researchers in a variety of ways.Although his presentations seemed to be spontaneous and often full of humor, they were always well thought out and delivered clear and important messages. In viewing one of my presentations the year of his death, he made many complementary remarks in email correspondence, but chided me for having too much information on my closing slide.He said that it was important to have a simple clear final message for each talk. A portion of his influence and success was due to many delightful professional and informal social interactions.When he liked a presentation, he would offer a simple “well done” and I very much valued such comments when I received them.At an American Chemical Society Meeting in New York City we went to the half price theatre ticket booth and chose to attend not a Broadway musical but a delightful Arthur Miller play with almost no audience.

5:00pm **AS+CA+HC+LS-WeA-9 The 'Crypto-Electron' Question: XPS of Tribo-electrified Insulators*, Hagai Cohen,*** Perlman bdg., The Weizmann Institute, Israel

Recent experiments on tribo-electrification have raised fundamental questions on the role of electrostatic charge in chemical and physical surface activity. Cryptolectrons were claimed to be created and, subsequently, be exploited to establish 'single-electrode electrochemistry'. However, our XPS study of this problem reveals methodological issues that were not taken into account. I will show that XPS proposes an interesting template for studies of various processes under controlled surface charge conditions, with which limiting factors on the magnitude of electrostatic surface fields can be extracted. How would a cryptoelectron, if existing, look like and can XPS imitate this creature to some extent – these questions and related ones will be discussed.

5:20pm **AS+CA+HC+LS-WeA-10 Effects, in XPS, on Composition Determination Using Different Background Removal Procedures: Single Crystal Fe_2O_3 as an Example*, Christopher R. Brundle,*** C R Brundle and Associates*; B. Crist,* xpsdata*; P. Bagus,* University of North Texas

Precision achievable in XPS is very good. Accurate quantitation from relative peak intensities is more difficult, even for homogenous materials. Normalizations for σ and λ are required, but the procedures are by now well understood. The accuracy of removing a background to establish the intrinsic spectrum is on less secure ground. There are several approaches, and implementation requires adjustment of parameters either manually, or automatically by the software used. The situation is at its most unsure when an XPS core level "peak" consists of overlapping structure spread over a wide (up to several 10's ev) BE range, such as with Fe 2p (multiplet splitting; shake structure) and O1s (shake) in Fe_2O_3 (1). The situation is similar for many other transition metal compounds. We examine, for a hematite single crystal, Tougaard and Shirley based background removals. Our conclusion is that the high BE endpoint, ie. where the person taking, or analyzing, the data sets the background to meet the experimental spectrum (implying there is no further intrinsic signal beyond that BE) is critical for high composition accuracy. Obviously, theory input on where intrinsic substructure ends helps to establish what is a reasonable endpoint (1). It is quite possible to adjust endpoints (Fe2p and O1s) to return the "expected" answer, 40% atomic Fe, but this is arbitrary, and, of course, assumes 100% accuracy of the relative σ and relative λ in addition to assuming a) that the Transmission Function, TF, of the instrument has been accurately calibrated, and b) that a small signal from surface OH is properly accounted for. So, in this presentation we are more concerned with the *range in composition* returned by each method (and variations within each method), rather than absolute values, when different, but plausible, endpoints are used. We also find that results differ using high energy resolution and low resolution. The two effects together amount to a ~4% variation in determined Fe %age for Tougaard and ~6% for Shirley. We stress that this work represents a practical approach, using the particular versions of the Tougaard and Shirley software available with the instrument involved, and no sample treatment within the instrument, which we believe is the way most practical XPS analyses are actually performed. Finally, we discuss the reasons for the differences observed and examine other possible procedures.

1) Origin of the complex main and satellite features in Fe 2p XPS of Fe_2O_3, Paul S. Bagus, Connie J. Nelin, C. R. Brundle, B. Vincent Crist, N. Lahiri, and Kevin M. Rosso, PCCP 2022 and references therein.

5:40pm **AS+CA+HC+LS-WeA-11 XPSOasis.org: the XPS Peak-Fitting Network*, Alberto Herrera-Gomez,*** CINVESTAV, Mexico*; D. Herrera-Rendon, E. Aguilar-Diaz,* RDATAA, Mexico

The XPSOasis Web platform aims to make available to the XPS community, free of charge, tools that facilitate communication between XPS users; this includes discussion forums, peak-fitting databases (one for each core-level), dynamic communication between users, and free data analysis software. The web platform allows users of different fitting software to easily upload posts to ask questions with images of the fitting that concern them. To answer the questions, the posts contain the data, allowing knowledgeable users to download and work on the recommendations.Novice users can consult expert users in direct conversations. Technical discussions on the analysis of XPS data can also be held. To hook expert (and non-expert) users, the participation is rewarded with *Spicer* points, which are accumulated through *likes* in their posts (given by other users) and when one of their posts reaches the peak-fitting data base (which is a decision of the corresponding moderator).Categories are defined in terms of the points.User belonging to certain categories can compete to become moderators of a certain core-level forum and database.They could also offer courses.Another advantage of having posts in the database is that they become the norm and could be cited.

The usefulness of XPSOasis.org is a function on the availability of peak-fitting parameters for each core-level for each element under a variety of chemical environments.Since it is a user-based platform, it becomes more useful as the number of users posts increases.This is a possible solution (which will, in fact, be provided by the XPS community itself) for the erroneous XPS analyses all too common in the scientific literature.

6:00pm **AS+CA+HC+LS-WeA-12 ASSD Peter Sherwood Mid-Career Award Talk: Advancing X-ray Photoelectron Spectroscopy (XPS) Methodologies for Materials Research*, Mark Biesinger*[1]**, Surface Science Western, Canada **INVITED**

Chemical state X-ray photoelectron spectroscopic (XPS) analysis of first row transition metals and their oxides and hydroxides is challenging due to the complexity of the 2p spectra resulting from peak asymmetries, complex multiplet splitting, shake-up and plasmon loss structure, and uncertain, overlapping binding energies. Our work has shown that all the values of the spectral fitting parameters for each specific species, i.e. binding energy (eV), full width at half maximum (FWHM) value (eV) for each pass energy, spin-orbit splitting values and asymmetric peak shape fitting parameters, are not all normally provided in the literature and databases, and are necessary for reproducible, quantitative chemical state analysis.

We have worked toward a consistent, practical, and effective approach to curve fitting based on a combination of 1) standard spectra from quality reference samples, 2) a survey of appropriate literature databases and/or a compilation of literature references, 3) specific literature references where fitting procedures are available and 4) theoretical fittings, where available, of multiplet split reference spectra. The use of well characterized standard samples and fitting of the entire peak shape has been shown to increase our ability to accurately identify and (semi) quantify the various species present in mixed oxide/hydroxide systems [1,2,3]. Additional chemical information has also been elucidated from Auger parameters and by using Wagner plots [4,5]. The unique spectral shapes of the LMM Auger peaks for these transition metals, particularly for Cu [5], have also been shown to be of use for chemical speciation. These methods have been shown to be effective in a wide variety of applications.

An overview of these curve-fitting methodologies will be presented along with examples highlighting how these methods have been used to elucidate complex sample chemistries.A recent assessment of available charge corrections procedures for insulating samples will also be shown [6].

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[1] **ASSD Peter Sherwood Award**

Applied Surface Science Division
Room 320 - Session AS+AC+BI+CA+HI-ThM

Unraveling the Composition of Complex Systems with SIMS

Moderators: Steve Consiglio, Tokyo Electron, **Gregory L. Fisher**, Physical Electronics

8:20am **AS+AC+BI+CA+HI-ThM-2 Ex-Situ, Surface and Bulk Investigations of Defluxing Chemistry Effects on Solder Mask*, J. Elliott Fowler,*** Sandia National Laboratories*; R. Gerhardt,* Georgia Institute of Technology*; J. Ohlhausen, R. Callaway,* Sandia National Laboratories*; M. Watt,* Georgia Institute of Technology*; S. Grosso, S. Rosenberg,* Sandia National Laboratories

Solder masking is an integral process in the manufacture of printed circuit board assemblies (PCBAs) – it serves to protect the unfinished copper traces from environmental effects, define the soldering pads and provide an adherable surface for conformal coating. Liquid photo-imageable (LPI) solder mask is one of the most popular choices for PCBAs due to ideal electrical and physical properties as well as chemical. LPI solder mask is a heterogeneous epoxy acrylate-based matrix, thus its surface chemistry can be very distinct from its overall bulk chemistry. The surface chemistry is of particular interest as it must be compatible with and resistant to a wide range of chemistries and environments which the PCBA will experience during its production and fielding lifetime. For instance, sensitivity to moisture is a well-known issue. Several studies of solder mask moisture absorption reveal that it reaches a saturation of ~1 weight percent in high-humidity environments, and corresponding changes in insulative properties occur. Risks to mask performance have arisen as a result of the use of new flux formulations which require increasingly aggressive aqueous defluxing chemistries for removal. We hypothesize that alkaline defluxing chemistries will significantly modify the surface chemistry of solder mask, making it more vulnerable to moisture and thus deteriorating their insulative properties.

A commercially available LPI solder mask material was prepared on squares of FR4 board and exposed to increasingly alklaine cleaning chemistries: including DI water, a pH neutral and a pH >10 defluxing chemistry. Samples were tested with three complementary surface-sensitive analytical techniques, x-ray photoelectron spectroscopy (XPS), time of flight secondary ion mass spectrometry (TOF-SIMS) and contact angle goniometry. TOF-SIMS results show that both pH neutral and alkaline chemistries alter the surface, removing PDMS and leaving organic residues. Contact angle goniometry shows that the alkaline chemistry makes the board's surface significantly more hydrophilic. XPS results show a decrease in Si at the surface correlating to a decrease in PDMS versus the control, with the largest decrease occurring due to the alkaline chemistry. In all cases, the surface is somewhat recoverable; however, recovery is less pronounced with increasing pH. AC impedance spectroscopy and DC Surface Insulation Resistance (SIR) testing of exposed samples in elevated humidity environments was performed to resolve changes in insulative performance due to observed changes in mask surface chemistry.

SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525

8:40am **AS+AC+BI+CA+HI-ThM-3 Unraveling the Composition of Complex Systems with SIMS*, Birgit Hagenhoff,*** Tascon GmbH, Germany **INVITED**

For more than four decades SIMS has proven to be a valuable tool in academic research as well as for industrial applications. Whereas the first years focussed on understanding the underlying physical processes using mono-elemental samples, the advent of ToF-SIMS (Time-of-Fligt Secondary Ion Mass Spectrometry) instrumentation in the 80s of the last century opened the path to using SIMS as a screening tool for characterising "the unknown", i.e. samples about which hardly anything is known before the analysis, where sample preparation should be as scarce as possible and where the analysis is performed without any chromatographic pre-step to separate out sample compounds.

Over the years, intensive discussions between those developing instruments and those applying them on a daily basis lead to a fruitful and steep learning curve in the SIMS communities. Meanwhile SIMS instruments offer a multitude of operational modes and are capable of analysing as 3D volume pixel by pixel. The lateral resolution has almost reached the physical limit of the collision cascade with values well below 100 nm and a depth resolution in the nm-range can be achieved. The development of cluster ion sources leads to the possibility to also probe organic materials in depth. At the same time data evaluation routines have become more powerful to address the large amount of data (several GByte for a 3D data set).

Generally, users would like to address three main questions: what (identification) is sitting where (localization) and how much is it (quantification)? Whereas the localization problem, as mentioned above, meanwhile is comparatively straightforward, identification and quantification still are challenging. In identification, the parallel presence of many elements and organic compounds in the SIMS spectra still asks for an expert to solve the analytical puzzle. Here, the application of multivariate statistical techniques and, more recently, machine learning approaching offer promising paths into the future. For a reliable quantification, the influence of the SIMS matrix effect on the results has to be taken into account. Here, the availability of suited reference samples plays a key role for closing the gap to quantitative techniques, like e.g. XPS (X-ray Photoelectron Spectroscopy).

The talk will therefore focus on identification and quantification issues including the use of multivariate statistics, MS/MS approaches and the use of reference sample comparing SIMS with the quantitative techniques XPS and LEIS (Low Energy Ion Scattering).

9:20am **AS+AC+BI+CA+HI-ThM-5 Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) as a Novel Approach to the Characterization of Coatings and Interfaces of Porous Transport Layers*, Genevieve Stelmacovich,*** *M. Walker, J. Foster,* Colorado School of Mines*; D. Cullen ,* Oak Ridge National Laboratory*; A. Paxson ,* Plug Power*; G. Bender, T. Schuler, S. Ware,* National Renewable Energy Laboratory*; S. Pylypenko,* Colorado School of Mines

The United States energy infrastructure aims to move towards the integration of hydrogen energy. As such, the production of reliable hydrogen generation through the optimization of water electrolyzers is imperative. In proton exchange membrane water electrolyzes (PEMWE's), the porous transport layer (PTL) plays an important role. Due to the harsh conditions of the cell, titanium is the current state-of-the-art anode PTL material. However, titanium quickly forms a layer of titanium oxide which significantly decreases conductivity of the PTL and respectively decreases the overall efficiency of the PEMWE system. To mitigate oxide effects, coatings are commonly applied to the PTL.

Focused Ion Beam Scanning Electron Microscopy (FIB-SEM) in conjunction with Scanning Transmission Electron MicroscopyEnergy-dispersive X-ray Spectroscopy (STEM-EDS) analysis is a commonly used technique to characterize PTL materials and PTL coatings, specifically to look at coating homogeneity and unfavorable oxide layer formation. Unfortunately, this approach is both time-consuming and labor intensive. Additionally, STEM-EDS analysis only provides elemental information, so if several oxide layers preside, it can be difficult to differentiate them, and thus lead to a lack of understanding fundamental degradation mechanisms. These technique deficiencies have motivated the development of an alternative approach that allow more efficient characterization of these materials. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is a valuable technique that is commonly used to characterize thin films and buried interfaces. ToF-SIMS can be performed relatively quickly, provides chemical information, and is sensitive to trace elements. This technique also enables visualization of elemental distribution, which provides more detailed surface and interface information. This presentation will demonstrate capabilities of ToF-SIMS for characterization of PTLs comparing results to TEM analysis of cross-sections obtained with FIB-SEM. This study will highlight similarities and differences between the techniques, expand on technique optimization for these morphologically challenging samples, and suggest paths for future investigation moving forward.

9:40am **AS+AC+BI+CA+HI-ThM-6 Construction of Accurate 3D NanoSIMS Depth Profiling Images of Cells in the Presence of Lateral Variations in Sputter Rate***, M. Brunet, B. Gorman,* ***Mary Kraft,*** University of Illinois Urbana-Champaign

We have developed a strategy for constructing accurate 3D NanoSIMSdepth profiling images of cells in the presence of lateral variations in sputter rate. In this strategy, we use the secondary electrons acquired in parallel with the negative ions during depth profiling to reconstruct the 3D morphology of the cell every time a depth profiling image is acquired. The morphologies created for each raster plane in the depth profile are adjusted to ensure that the height at every pixel decreases with increasing image plane. The resulting reconstructions of the cell's morphology are used to define the z-positions of the voxels in the component-specific 3D NanoSIMS images. We validated this strategy by comparing morphology reconstructions for secondary electron depth profiling images acquired with focused ion beam - secondary electron microscopyand AFMdata acquired from the cell before depth profiling. The shape, curvature, and relative height of the reconstructed morphology agreed well with the AFM data. Depth correction of 3D NanoSIMSdepth profiling data of a metabolically labeled mammalian cell using this strategy improved visualization of the^{18}O-cholesterol and ^{15}N-sphingolipids distributions intransport vesicles and organelle membranes. Accurate 3D NanoSIMS images that show the intracellular distributions of molecules of interest may now be constructed in the presence of variations in sputter rate and the absence of correlated topography data.

11:00am **AS+AC+BI+CA+HI-ThM-10 Innovations in Nuclear Materials Analysis with SIMS*, Christopher Szakal,*** National Institute of Standards and Technology (NIST) **INVITED**

Global nuclear safeguards efforts, coordinated by the International Atomic Energy Agency (IAEA), require precision measurements to answer questions related to nuclear treaty compliance. Despite those questions seeming relatively simple, and the elemental composition of the target analytes often consisting of just uranium and oxygen, the complex processes employed to answer those questions reveal the importance of subtle nuances to meet analytical objectives. This presentation will explore the complexity of this type of analyte system and how innovations in secondary ion mass spectrometry (SIMS) resulted in a routinely utilized tool to address nuclear safeguards requirements for environmental sampling analysis. The complexity is largely driven by the small amounts of nuclear particle material available for analysis, including challenges for 1) representative sampling of analyte material to represent actual nuclear processes, 2) accuracy and precision of uranium isotopic analyses across a wide dynamic range, and 3) determining when a nuclear process created the analyte material. Precision SIMS measurements provide the opportunity to address these analytical complexities to answer key nuclear safeguards questions, but the presentation will also highlight when limitations are inevitable for which questions can be answered.

11:40am **AS+AC+BI+CA+HI-ThM-12 Understanding Surface Bonding and Molecular Structure with MS/MS Imaging: From Click-Chemistry to Biogenesis*, Gregory L. Fisher,*** Physical Electronics

A TOF-TOF imaging mass spectrometer allows TOF-SIMS (MS^1) imaging and tandem MS (MS^2) imaging to be achieved in a lossless fashion [1,2]. Secondary ions for MS^1 and MS^2 analysis are produced from the same surface area by a primary ion nanoprobe. Monolayer film samples may be characterized without undesired erosion or degradation; even sub-monolayer 2D films are readily characterized. Kilo-electron volt collision-induced dissociation (keV-CID) enables compositional identification and structural elucidation of precursor ion moieties. This analytical capability has been brought to bear for straightforward molecular identification as well as multifaceted studies involving surface modification, polymers, composites, catalysis, forensic and failure analysis, biology and pharmaceuticals. TOF-SIMS tandem MS imaging was employed to unravel the click-chemistry of sub-monolayer films [3] and shed new light to unlock the mystery of molecular biogenesis [4,5].

References

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

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

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

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

12:00pm **AS+AC+BI+CA+HI-ThM-13 Probing Grain Boundary Segregation in 304L Stainless Steel using Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)*, James Ohlhausen,*** *E. Barrick, D. Susan, C. Robino, K. Hattar, J. Herrmann, P. Duran, J. Rodelas,* Sandia National Laboratories

Boron-rich phases in austenitic stainless steels can promote liquation cracking in the heat affected zone during welding. Stainless steels with boron concentrations even as low as 20 wt. ppm are susceptible to grain boundary cracking after heat treatments. The kinetics of phase transformations during heat treatment that generate the crack susceptible microstructure are currently unknown. Time-of-flight Secondary Ion Mass Spectrometry (ToF-SIMS) was used to map Boron at grain boundaries and in the bulk at trace levels for a series of 304L stainless steel coupons that were heat treated across a range of temperatures and cooling rates to investigate these phase transformations.ToF-SIMS and Scanning electron microscopy (SEM) were used to observe the distribution of chromium borides before and after heat treatment. These results will be used to enable quantitative prediction of thermal processing conditions to avoid weld cracking.Sample preparation methods, ToF-SIMS acquisition conditions and data analysis will be discussed.

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Surface Science Division
Room 320 - Session SS2+CA+AS-FrM

Environmental, Atmospheric and Astronomical Surfaces

Moderators: Kathryn Perrine, Michigan Technological University, **Xiao-Ying Yu**, Oak Ridge National Laboratory, USA

8:20am **SS2+CA+AS-FrM-1 Combining Synchrotron X-ray and SFG Spectroscopy Techniques to Illuminate Aqueous Interfaces***, S. Nayak, R. Kumal, A. Carr,* Argonne National Laboratory, USA*; S. Lee,* Argonne National Laboratory*; **Ahmet Uysal,*** Argonne National Laboratory, USA **INVITED**

Chemical separations are central to our energy, environment, and security needs. From efficient refinery and recycling of rare earths to cleanup of contaminated underground waters, chemical separations cover a wide range of processes such as liquid-liquid extraction (LLE), membranes, and sorbents. A common theme in most processes is that the target ions need to adsorb on or go through an interface. Understanding aqueous interfaces at molecular scale, require special experimental techniques that can distinguish the interfacial structures from the overwhelmingly larger bulk.

Surface sensitive synchrotron X-ray scattering and fluorescence, and vibrational sum frequency generation (SFG) spectroscopy techniques are among the most advanced tools available to study aqueous interfaces. Interestingly, these techniques have been developed in separate communities and there are only a handful of studies that take advantage of complementary nature of them. In this presentation, I will summarize our group's efforts in understanding aqueous interfaces in chemical separations, by combining these two experimental techniques. I will provide specific examples where a single method is not enough to decipher the complex interactions at the interface. The examples cover ion-amphiphile interactions in LLE [1-4] and ion adsorption on graphene-oxide thin films [5].

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2.Kumal, R. R.; Nayak, S.; Bu, W.; Uysal, A., Chemical Potential Driven Reorganization of Anions between Stern and Diffuse Layers at the Air/Water Interface. J. Phys. Chem. C 2021.

3.Kumal, R.; Wimalasiri, P.; Servis, M.; Uysal, A., Thiocyanate Ions Form Antiparallel Populations at the Concentrated Electrolyte/Charged Surfactant Interface. ChemRxiv 2022, https://doi.org/10.26434/chemrxiv-2022-x8s7x

4.Nayak, S.; Kumal, R. R.; Uysal, A., Spontaneous and Ion-Specific Formation of Inverted Bilayers at Air/Aqueous Interface. Langmuir 2022, https://doi.org/10.1021/acs.langmuir.2c00208

5.Carr, A. J.; Kumal, R. R.; Bu, W.; Uysal, A., Effects of ion adsorption on graphene oxide films and interfacial water structure: A molecular-scale description. Carbon 2022, 195, 131-140.

9:00am **SS2+CA+AS-FrM-3 X-Ray Studies of Extractant and Lanthanide Ion Ordering at Liquid Interfaces Relevant to Solvent Extraction***, **Mark Schlossman,*** University of Illinois at Chicago **INVITED**

Solvent extraction processes are designed to extract a target species of ion from a multi-component aqueous mixture into an organic solvent, then return it to an aqueous phase containing only the targeted species. Ongoing developments of solvent extraction processes are aimed at optimizing the efficiency and kinetics of the separation and recovery of base, rare earth, and precious metals, as well as the reprocessing of spent nuclear fuel and nuclear waste. During solvent extraction, extractants and complexants assist the transport of metal ions across the liquid-liquid interface between an aqueous solution and an organic solvent. Complexation of metal ions with extractants and complexants is believed to take place at or near the organic-aqueous interface, as demonstrated recently by synchrotron x-ray measurements which locate and characterize metal ions and their complexes in the liquid-liquid interfacial region. This presentation will describe recent X-ray studies of model liquid interfacial systems relevant to the extraction of rare earth ions. These results suggest a connection between the observed interfacial structures and the extraction mechanism, which ultimately affects the extraction kinetics.

9:40am **SS2+CA+AS-FrM-5 Probing Surface Chemistry in Complex Environments: Water Disinfectants and Ionic Solutions at the Air/Liquid/Iron Interface***, **Kathryn Perrine,*** Michigan Technological University

Water disinfectants are used to treat pathogens in the water supply, but chlorine is known to react with organic matter to produce toxic disinfectant by-products (DBP). Other disinfectants, such as monochloramine, provide a higher level of disinfection without producing chlorinated DBP's. However, studies have shown that monochloramine can corrode copper and lead surfaces, but little is known for iron-based materials. Iron interfaces are prevalent in soils, minerals, and atmospheric dust, and are known to undergo redox reactions. Iron is a known catalyst in several processes due to its different active sites. Due to the advent of degradation of disinfectants in the water supply, the reaction of monochloramine was investigated on iron interfaces in complex environments.

The interaction of monochloramine was studied at the air/solution/iron interface using *in situ* polarized modulated infrared reflection absorption spectroscopy (PM-IRRAS). These studies are compared with the iron interfaces exposed to aqueous solutions that were used to synthesize monochloramine, NH_4Cl(aq), NaOH(aq), and NaOCl(aq). After exposure to each solution, ATR-FTIR spectroscopy and X-ray photoelectron spectroscopy were used to measure the chemical composition at the interface region exposed to atmospheric O_2 and CO_2 and the region submerged in solution. This builds upon our previous work where we have investigated alkali and alkaline chloride solutions at the air/electrolyte/iron interface. There the anion acts to corrode the surface to produce nucleation sites for carbonate film growth, while the cation influences the mineral film identity and the rate of carbonation from the uptake of CO_2. These findings show that water disinfectants at solution/metal interfaces result in unexpected reactions in complex aqueous systems, which may provide insight for related surface catalytic and environmental processes.

10:00am **SS2+CA+AS-FrM-6 The Surface Chemistry of Martian Mineral AnalogsDuring Triboelectric Charging in Sand Storms***, **Mikkel Bregnhøj,** T. Weidner, K. Finster,* Aarhus University, Denmark

The surface chemistry of the Martian regolith has a significant impact on the atmospheric composition on the Red Planet. For example, methane concentrations vary by a factor of ~3 or more during a Marsian year. Theories based on established photochemical and environmental mechanisms, have so far failed to accurately model the seasonal variation. The currently known gas/solid interfacial chemistry that forms and removes methane from the Marsian atmosphere is insufficient to explain the observed dynamics.

We propose an alternative driver of Martian surface chemistry: wind-driven triboelectric charging of minerals. Sand storms, saltation, and erosion are common phenomena on the Red Planet. In proof-of-principle laboratory experiments, we have shown how Martian mineral analogs can erode each other and induce electric discharges with sufficient energy to (1) ionize and/or dissociate gasses like argon, methane, and carbon dioxide and (2) drive gas/solid interfacial chemistry of organic species present on the surface of these minerals. Using advanced surface spectroscopies (XPS, NEXAFS, etc.) we show how saltation can drastically alter the gas and mineral surface composition. For example, tumbling quartz sand in a methane atmosphere will change the colour of the sand from pristine white to reddish/brown (see attached figure). Using a custom-built container, we also simulate a sand storm with realistic Martian atmospheres and mineral analogs, sealed inside a container made of the very same mineral. In this way, we exclude possible interference effects from the container walls, and come as close to the actual conditions of a sand storm on Mars as is possible on Earth.

10:20am **SS2+CA+AS-FrM-7 Unraveling Water Formation on Planetary and Astrophysical Bodies: The Role of Surface Science***, T. Orlando, **Brant Jones,*** Georgia Institute of Technology **INVITED**

The sources of molecular water in planetary systems is a subject of general interest in astrophysics and astrochemistry and its presence and persistence are critical for life on Earth and for space missions involving long term human exploration.The Moon is the nearest exploration target and sources of water include primordial water, delivery via comets and meteorites, formation and release during small impact events, and solar wind interactions. Our controlled surface science experiments have demonstrated that thermally activated recombinative desorption (RD) or associative desorption (AD) from lunar regolith and other solar wind irradiated grains can be an additional source term for water formation. This involves hydroxyl (-OH) defects made by implantation of solar wind protons. Using several Apollo lunar samples, temperature program desorption (TPD) experiments conducted under ultra-high vacuum conditions yielded first order activation energies for desorption of chemisorbed molecular water and second order activation energies for the RD mediated formation and release of molecular water. Depending on the temperature excursions, RD can occur on a diurnal basis on the Moon and is likely prevalent during impacts with meteorites and meteoroids. This is simulated by laser impact studies followed by state and velocity resolved detection of the photo-produced water. Once formed, the water can either desorb, or be transported on and within the regolith and grain surfaces.Our combined experimental and modeling effort has successfully simulated recent observational data of water on both Mercury and the Moon. Water formation via RD is also likely general under astrophysical conditions that involve proton bombardment followed by thermal excursions (> 400 K), and is critical to the formation of water in star forming regions and in developing strategies for extraction of water for future, sustainable human space exploration missions.

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