

## Chemical Analysis and Imaging of Interfaces Room Central Exhibit Hall - Session CA-ThP

### Chemical Analysis and Imaging of Interfaces Poster Session

**CA-ThP-1 Multimodal in-Situ Characterization of Fe Anode for Aqueous Battery, Xiao Zhao**, Lawrence Berkeley National Laboratory; *E. Carlson, A. Burgos, W. Chueh*, Stanford University

Metallic iron is an attractive anode material for aqueous batteries, particularly if the full 3-electron redox between Fe and Fe (III) can be accessed reversibly. However, oxidation of Fe (II) to Fe (III) causes drastic morphology change and irreversible formation of highly resistive phases. Yet, it remains unclear how these phases form at the nanoscale and, crucially, how they might be avoided. To achieve fully reversible Fe anodes, it is critical to obtain a mechanistic understanding of nanoscale morphology and phase evolution during electrode cycling. Here we investigated the electrochemical transformation pathways between Fe (0)/Fe (II) and Fe (III) oxides using various in-situ spectroscopic and microscopic techniques, including Raman, Electrochemical Atomic Force Microscopy (ECAFM), soft X-ray Absorption Near Edge Structure (XANES), Infrared Nanospectroscopy (nano-FTIR) and Scanning Transmission X-ray Microscopy (STXM). Correlating the morphological evolution during this transformation to local (and surface) Fe oxidation state, phase and conductivity offers fundamental insight into Fe (0/II)/(III) conversion and inspire novel engineering of the Fe anode to achieve higher capacity and cyclability.

**CA-ThP-2 Off-axis EELS Bandgap Measurements at Complex Oxide Interfaces, Kory Burns**, University of Virginia, USA; *J. Hachtel, J. Poplawsky*, Oak Ridge National Laboratory, USA

Complex oxide interfaces have captivated the research community in the last 15 years due to the potential emergent nanoscale phenomena, owing to the strong interaction among charge, spin, orbital, and structural degrees of freedom. Studying these interfaces across a few unit cells is challenging with conventional methods, as optical probes tend to be around 1  $\mu\text{m}$  in diameter. This makes it's impossible to study an individual interface of a vertically stacked transition metal oxide from a cross-sectional sample as the optical probe collects an averaged signal from each layer. In this talk, electron probes are used to overcome the diffraction-limit set by optical probes. This is done by converging electrons to a focused beam to collect spectroscopic signal from an oxide-interface with electron energy loss spectroscopy (EELS). A monochromated aberration corrected scanning transmission electron microscopy (MAC-STEM) is used to couple unprecedented energy resolution and spatial resolution to do vibrational spectroscopy at atomic resolution. When the EELS aperture is in conventional settings, where the bright field disc is perfectly aligned with the entrance aperture, the EELS signal is delocalized and dominated by optical selection rules. Accordingly, the bright field disc is electrostatically shifted by the projector lens so that the dark field disc is highlighted, which describes a technique known as off-axis EELS. We use this to create a localized signal dominated by impact scattering so that the long-range contributions are suppressed, and band edges can be resolved without plasmon interference. Ultimately, we aim to introduce a novel technique to determine the structure-property relationship of complex oxides to bring oxide-electronics to new heights.

**CA-ThP-3 ToF-SIMS Analysis of Biofilms after Overlayer Removal by fs-Laser Ablation, Gabriel Parker**, A. Karaginnakis, R. Shavandi, University of Illinois - Chicago; *X. Yu*, ORNL; *L. Hanley*, University of Illinois - Chicago

The biological secretions from bacterial biofilms contain fatty acids, metabolites, and other components of the extracellular polymeric substances (EPS). These secretions can result in corrosion of hard surfaces. Fatty acids produced by *Paenibacillus* sp. 300A, *Acidovorax* JHL-9, and *Shewanella ondenensis* MR-1 are thought to degrade glasses, polymers, and other materials. Observation of these fatty acids and other metabolites like quinolones, flavonoids, and quorum sensing molecules help reveal the metabolic process that can contribute to material degradation. The depth profiling capabilities of ToF-SIMS are particularly useful for distinguishing processes at the air-biofilm interface from those at the biofilm-material interface. However, ToF-SIMS depth profiling by gaseous cluster ion beams is only reliable for elucidating biofilm composition and structures down to a depth of a few micrometers and biofilms can grow to thicknesses surpassing a millimeter [1]. Ablation with 800 nm, ~75 fs laser pulses (fs-LA) has used for layer removal and depth profiling at much greater depths and without damage to the underlying biofilm [2, 3]. Femtosecond-LA

combined with X-ray photoelectron spectroscopy has also been demonstrated for depth profiling in polymers [1]. Stand-alone fs-LA is used here to expose buried regions of biofilms of *Paenibacillus* sp. 300A biofilms cultured on Si wafers and other substrates for analysis using ToF-SIMS. Comparison of the mass spectra of ablated vs. non-ablated regions shows an absence of laser-induced changes in their respective chemical compositions, demonstrating the feasibility of fs-LA for probing buried regions of biofilms that are not readily accessible to gaseous cluster ion beams.

[1]M.A. Baker... R.G. White, Appl. Surf. Sci. 654 (2024) 159405.

[2]S. Milasinovic,... L. Hanley, J. Vac. Sci. Technol. A 28 (2010) 647.

[3]Y. Cui,... L. Hanley, ACS Appl. Mater. Interf. 5 (2013) 9269.

**CA-ThP-4 Breakdown Failure Analysis of Diamond Lateral Schottky Barrier Diode Device Using EBIC-Based Metrology, Andrei Kolmakov**, NIST-Gaithersburg; *Z. Han, J. Lee*, UIUC; *K. Cheung, E. Strelcov, O. Ridzel, J. Villarrubia, G. Holland*, NIST-Gaithersburg; *C. Bayram*, UIUC

Diamond ca 5.5 eV wide band gap, high (> 20 W /cm K) thermal conductivity, carrier mobility (>2000 cm<sup>2</sup> /V s) and critical electric field (> 10 MV/cm make it an ideal material for emerging high-power electronics. For these applications, the development of the diodes with highest breakdown voltage is a requirement. The analysis of the breakdown mechanism and leakage channels in diamond devices however remains to be an experimental challenge. Electron beam induced current microscopy (EBIC) is often used to characterize the imbedded/induced electric field distributions at the surface as well as buried interfaces and obtain the current maps in semiconductor devices. In this report, the combined electrical and EBIC measurements were applied to the same p-type lateral Schottky barrier diamond diode before and after its soft breakdown. This allowed to univocally identify the development of the device leakage channels and relate them with device fabrication defects.

**CA-ThP-5 Oxide Layer Characterization of Superconducting Two-layer Tin Films: Al/Nb and Al/Nb-Ti-N on Silicon, G. Bhandari, V. Dewasurendra, F. Akinrinola, J. Metzger, A. Sheppard**, West Virginia University, USA; *T. Stevenson, E. Barrentine, L. Hess*, NASA Goddard Space Flight Center; *M. Johnson, Micky Holcomb*, West Virginia University, USA

Superconducting devices are important for the detection of microwave to x-ray radiation. Identifying the factors affecting oxide thickness, uniformity, and chemical composition will lead to the development of more reliable and lower noise detectors. We compare x-ray absorption spectroscopy (XAS) measurements and depth-dependent x-ray photoemission spectroscopy (XPS). We have studied two types of superconducting thin films: Al/Nb and Al /Nb-Ti-N. Depth-dependent niobium oxide (Nb<sub>2</sub>O<sub>5</sub>, NbO<sub>2</sub> and NbO) formation has been evaluated. We explore the impact of different etching and oxide cleaning treatments to the presence of these oxides. This research is supported by NASA EPSCoR Award# 80NSSC22M0173. We acknowledge the use of the research facilities at the Lawrence Berkeley National Laboratory and West Virginia University Shared Research Facilities.

**CA-ThP-6 Deep Probing of Buried Layers with HAXPES - Chemical Analysis with Bias Applied Operando Setup for Electronic Devices, Marcus Lundwall**, T. Sloboda, Scienta Omicron, Sweden; *D. Beaton*, Scienta Omicron; *M. Machida*, Scienta Omicron, Japan

#### Introduction

Buried interfaces in electronic devices such as batteries, solar cells, transistors etc. are highly chemically sensitive and reliable instrumentation is necessary for material development. While X-ray photoelectron spectroscopy (XPS) is a powerful method to investigate the chemical nature of surfaces, buried interfaces in device electronics are more difficult to investigate due to scattering. Hard X-rays giving increased information depth, have therefore been increasingly used in the photoelectron spectroscopy field.

#### HAXPES and XPS applications

Having access to XPS and HAXPES X-ray sources enables measurements of core levels with different resulting kinetic energy of the photoelectrons. With a soft X-ray XPS source, the kinetic energy is low and thus the obtained information is very surface sensitive. With Hard X-rays it is possible to be both surface and bulk sensitive, as electrons stemming from deep core levels will have lower kinetic energy and contain more surface sensitive information. Similarly, electrons stemming from shallow "XPS" core levels will have higher kinetic energy and contain more bulk sensitive information. This is especially valuable when detecting artefacts formed by sample exposure to different environments (e.g. air, moisture, heat, cold

etc.) or by preparation steps known to induce chemical changes on the surface (e.g. sputtering). Scienta Omicron's HAXPES Lab uses both an XPS Al K $\alpha$  source and a monochromatic Ga K $\alpha$  MetalJet HAXPES source with excitation energy of 9.25 keV, therefore enabling artefact-free investigations with superior information depth, which clearly extends beyond limits of conventional XPS surface analysis. This unlocks a comprehensive and effective characterisation of layered materials. Combined with a hemispherical electron analyzer with a  $\pm 30$  degree acceptance angle, investigation of buried interfaces, operando devices and real-world samples becomes achievable. (Fig.1). Over the years it has proven invaluable in research of semiconductor materials in thin film electronic devices including the operando characterization of bias induced changes in chemical composition of material interfaces. Other applications include polymer materials, metal surfaces and coatings. This presentation will give an overview of HAXPES applications with focus on buried interfaces in electronic devices such as passivation of luminescent quantum dots studied through a 35 nm overlayer, and semiconductor device band alignment by operando measurement with the Si substrate signal as reference detected through 20 nm TiN + 4 nm ZrO stack without sputtering and risk of artifacts.

**CA-ThP-7 Stability and Dielectric Strength of Model Metal/Al<sub>2</sub>O<sub>3</sub>/Diamond Interfaces Under Harsh Environments**, *J. Trey Diulus, A. Biacchi, E. Bittle, A. Kolmakov, NIST-Gaithersburg*

Recent progress towards innovation in power electronics has largely been through implementation of new wide-bandgap (WBG) semiconductor materials, like SiC or GaN. Alternatively, diamond is another WBG material with a high theoretical hole mobility ( $1300 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ ), thermal conductivity, and breakdown voltage that rivals SiC and GaN, while also offering improved chemical and thermal stability over its WBG counterparts. Recently, diamond electronic devices have been fabricated displaying impressive electrical performance and thermal management, however little has been investigated for these model devices at high temperatures in combination with heavily oxidizing or reducing ("harsh") environments. In this work, we fabricated model diamond devices that possess metal/Al<sub>2</sub>O<sub>3</sub>/metal/diamond, and metal/Al<sub>2</sub>O<sub>3</sub>/diamond interfaces by depositing the standard metal contact stack (Ti/Pt/Au) or pure Pt on undoped and non-hydrogenated diamond followed by growth of a 40-50 nm Al<sub>2</sub>O<sub>3</sub> film via ALD as a gate dielectric. We then investigated the dielectric properties of this un-gated device by conducting I-V and capacitance measurements prior to any exposure. Next, the sample surface chemistry and morphology are investigated with x-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM), respectively. The device is then annealed to 600 °C, followed by exposures to H<sub>2</sub> and O<sub>2</sub> partial pressures of up to 10 kPa also at elevated temperature, where XPS, SEM, and 2-point I-V are all collected at each intermediate step *in situ* without breaking vacuum. Overall, we defined the stability range of a model diamond interfaces at high temperature and reactive environments.

**CA-ThP-8 Profiling Ultrathick Films using Argon Clusters – Characterizing Polystyrene Microsphere Standards as Surrogates for Pharmaceutical Particles inside Drug Delivery Films**, *Shin Muramoto*, national institute of standard and Technology

For thin organic films, argon cluster sputtering enables molecular depth profiling with minimal topography generation or changes in sputter rate. However, for ultrathick films (>10  $\mu\text{m}$  of sputtered depth) we have observed the rapid formation of micron-scale pillars that significantly affect both the linearity of the sputter yield and depth resolution. For example, sputtering of gelatin using an ion dose of  $7 \times 10^{16} \text{ ions/cm}^2$  resulted in the formation of 42  $\mu\text{m}$  deep craters with 20  $\mu\text{m}$  tall pillars on the crater bottom, pointed at 45° towards the cluster source and formed through masked sputtering from impurities in the film. When the pillars reached a threshold number on the crater bottom, the sputter yield was seen to slow, which led to distortions in the 3D image – the depth resolution at the film-sphere interface would change from  $(7.1 \pm 1.6) \mu\text{m}$  to  $(9.4 \pm 3.2) \mu\text{m}$  at sputtered depths of roughly 10  $\mu\text{m}$  and 20  $\mu\text{m}$ , respectively. To accurately compensate for this artifact, especially for the imaging and sizing of drug particles, (5, 10, 20, and 40)  $\mu\text{m}$  polystyrene (PS) sphere standards were embedded in single component films of gelatin, polyvinylpyrrolidone (PVP), cellulose, acrylic acid, and pullulan (which are major components in oral drug delivery films) to study how sputtered depth affects the overall shape of the spheres. Certain matrices also showed a suppression of the signal, such as PVP and pullulan, which made visualization of 5  $\mu\text{m}$  spheres difficult and put a size limit on the detectable size of the spheres. And for the case of acrylic acid, mass interference at  $m/z$  91 (base peak for PS) forced the use of much lower intensity PS peaks which further degraded the depth resolution. This work outlines the challenges of 3D imaging of ultrathick

films, with an emphasis on how surface topography affects the representation of the objects embedded in ultrathick films, with the ultimate goal of extending this study to the accurate imaging of pharmaceutical particles inside oral drug delivery films.

**CA-ThP-9 Differential Ion Movement is Captured by XPS under Voltage-Bias through a Multi-Layered-Graphene Electrode in contact with a Mixed Ionic Liquid Medium**, *E. Kutbay*, Bilkent University, Chemistry Department, 06800 Ankara, Turkey; *F. Krebs, O. Hoefft, F. Endres*, Clausthal University of Technology, Germany; *Sefik Suzer*, Bilkent University, Chemistry Department, 06800 Ankara, Turkey

Under application of a voltage bias, asymmetric ion-movement of a mixed ionic liquid (IL), having the same anion [bis(trifluoromethylsulfonyl)imide / TFSI<sup>-</sup>] but two different cations [1-butyl-1-methylpyrrolidinium / BMP<sup>+</sup> and Rb<sup>+</sup>] through a multi-layered graphene (MLG) electrode, has been detected by x-ray photoelectron spectroscopy (XPS), via recording the intensities of the C1s, N1s, F1s and Rb3d core level peaks. Accordingly, upon increasing the bias gradually from 1 to 3.5 V, we have observed up to 3-fold increase in the Rb3d peaks signal, accompanied with parallel F1s and N1s peak intensity changes, albeit to a lesser degree. The C1s peak of the graphene layer was observed to decrease, clearly indicating the increase in the surface composition of the IL. Moreover, a discernable differential change in the N1s peaks of the anion (N<sup>-</sup>) and the cation (N<sup>+</sup>) was also observed. Additionally, bias dependent binding energy shifts, extracted through the changes in the positions of F1s, N1s and C1s and Rb3d peaks of the IL mixture and the C1s of the graphene electrode indicate that multi-faceted and distinct solid-liquid interfaces develop throughout the entire intercalation process with an additional and pertinent evidence for finite potential drops. Details of the experimental set-up, and dynamics of bias-induced ion movement will be presented and discussed.

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