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.

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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.

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

[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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