Applied Surface Science
Room: 212D - Session AS+SS-WeA

Characterization of Buried Interfaces
Moderator: Xia Dong, Eli Lilly and Company, James Ohlhausen, Sandia National Laboratories

2:20pm **AS+SS-WeA1 ASSD 30th Anniversary Speaker: Characterization of Sub-surface Interfaces using SIMS, TEM, and FIB or: How Much will it Cost me to Fix that Interface?**, ***Fred Stevie***, North Carolina State University **INVITED**

Characterization of interfaces between layers or between layer and substrate has always been of interest. Interface issues include visible problems, such as delamination or corrosion, and contamination that can affect product quality, such as electrical properties in semiconductors. The information desired includes the physical quality of the interface and identification and quantification of contaminants. This presentation summarizes multiple approaches to interface analysis, particularly with use of SIMS, FIB, and TEM.

Common approaches for analysis of a buried interface involve a depth profile or cross section. Depth profiling by SIMS is often used because of good sensitivity and depth resolution. Matrix, dopant and contaminant species in the structure can be characterized with a single SIMS depth profile. Quantification of contamination at an interface is highly desired but can be difficult to obtain. Once an element has been identified as a contaminant, quantification at interfaces may be possible with ion implantation. Significant improvements have been made with the species used for depth profiling. C_{60} and argon cluster beams are used to depth profile organic materials. These high mass ion beams provide better sensitivity for high mass species and do not affect the chemical composition, so it is possible to obtain interfacial chemistry.

The FIB has revolutionized sample preparation and lift-out methods can routinely prepare cross section specimens for TEM analysis. A sample polished to provide an edge can rapidly be trimmed with FIB to provide a surface 50 to 100µm in height that is suitable for high resolution analysis. Optimization of beam conditions such as dwell and overlap can increase removal rate by several times. Plasma ion sources dramatically increase material removal rates and make possible the study of 100µm deep interfaces which will cover most layers of interest. Plating coatings are commonly less than 5µm thick and paint coatings 100 to 150µm.

3:00pm **AS+SS-WeA3 FIB-TOF Tomography Characterization of Organic Structures**, ***David Carr***, *G.L. Fisher,* Physical Electronics USA, *S. Iida, T. Miyayama*, ULVAC-PHI

1. Introduction

There are practical limitations to the use of ion beam sputtering for probing the sample chemistry beyond the surface region which include preferential sputtering and accumulated sputter beam damage. Both effects result in a distortion or complete loss of the true 3D chemical distribution as a function of depth

An alternative approach to achieve 3D chemical imaging of complex matrix chemistries is to utilize *in situ* FIB milling and sectioning in conjunction with TOF-SIMS chemical imaging, or 3D FIB-TOF tomography [1]. This can minimize or eliminate artifacts caused by sputter depth profiling such as differential sputtering and accumulated ion beam damage.

However, even with FIB polishing there remains some FIB beam-induced chemical or molecular damage that may or may not limit the detection of characteristic molecular signals. For certain specimens, it is an advantage to follow FIB polishing with cluster ion polishing to recover the characteristic molecular signals.

2. Method

The 3D chemical characterization of pure organic and metal-organic mixed composition structures was achieved utilizing 3D FIB-TOF tomography on a PHI TRIFT *nanoTOF* II (Physical Electronics, USA) imaging mass spectrometer. The spectrometer's large angular acceptance and depth-of-field maintain high mass resolution and high mass scale linearity even in this challenging geometry. This provides the highly desirable ability to perform artifact-free chemical imaging of high aspect ratio features.

3. Results

The present study investigated samples from two classes of materials: one metal-organic mixed matrix composition and one mixed organic phase comprised of two polymer moieties. Since there was no preferential sputtering, an immediate result of the FIB-TOF imaging was the accurate determination of the depth scale. We have collected characteristic molecular information from each sample for the purposes of 2D and 3D imaging. Cluster ion beam polishing (e.g. C_{60}^{+} or $Ar_{2,500}^{+}$) was necessary to remove the FIB beam-induced damage, and the new instrument configuration allows cluster ion polishing to be accomplished with ease. We will highlight certain aspects of the studies for presentation.

4. References

[1] A. Wucher, G.L. Fisher and C.M. Mahoney, Three-Dimensional Imaging with Cluster Ion Beams (p. 207-246) in *Cluster Secondary Ion Mass Spectrometry: Principles and Applications*, C.M. Mahoney (Ed.), Wiley & Sons, N.J. (2013).

4:20pm **AS+SS-WeA7 Interface Characterization using Ballistic Electron Emission Microscopy and Spectroscopy: Recent Results and Related Techniques**, ***Douglas Bell***, Jet Propulsion Laboratory, California Institute of Technology **INVITED**

Ballistic electron emission microscopy (BEEM) is a microscopy and spectroscopy based on scanning tunneling microscopy (STM), developed as a scanning probe of subsurface interface properties. By monitoring the fraction of tunneling current between STM tip and sample that traverses a subsurface heterostructure, BEEM can probe hot-carrier transport as well as heterostructure and material properties. Because BEEM uses an STM tip to inject a highly localized carrier distribution, high-resolution imaging of interface electronic structure can be performed. Control of tunnel voltage polarity allows injection of either holes or electrons into the sample structure, thus enabling characterization of electronic structure both above and below the Fermi level.

Since its inception, BEEM has found many applications such as studies of interface heterogeneity, carrier scattering, band structure, transport in oxides, and interface chemistry. A wide range of structures have been probed, including metal/semiconductor, metal/oxide/semiconductor, quantum wells, and quantum dots. Researchers have measured quantized energy levels and spatial variations of Schottky barrier height. BEEM has also provided a new means for studying fundamental characteristics of interface transport such as conservation of momentum parallel to an interface.

More recently, BEEM has been applied to the investigation of other novel materials and structures. Organic materials, graphene layers, and nanowires have received attention, and research has been done on molecular vibrational spectroscopy. Related techniques for magnetic materials, and measurements of BEEM-induced luminescence, have been further developed and demonstrated.

This talk will discuss some of these recent advances and extensions, as well as further developments in more traditional areas. Some comparisons with results from other characterization techniques will also be presented.

5:00pm **AS+SS-WeA9 Using XPS to Study Electrochemical Solid-Liquid Interfaces In-Operando: Standing-Wave Ambient-Pressure XPS (SWAPPS)**, ***Osman Karslioglu***, Lawrence Berkeley National Laboratory, *S. Nemsak,* Forschungszentrum Juelich GmbH, Germany, *I. Zegkinoglou, A. Shavorskiy, M. Hartl, C.S. Fadley, H. Bluhm*, Lawrence Berkeley National Laboratory

Accessing the chemical and electrical potential information at a solid/liquid interface is an important capability for investigating a process like corrosion where electrochemical transformations are at work. Here we report the first results of a combination of techniques, where we use X-ray standing waves to enhance the photoemission signal from the solid-liquid interface during an ambient-pressure XPS experiment, investigating the oxidation of Ni. X-ray standing waves were generated by a Si/Mo multilayer mirror, on which the sample is prepared as a thin layer (~8 nm Ni in this case). A thin liquid layer was formed on the surface by dipping the sample into an electrolyte (KOH(aq), 0.1 mol/L) and pulling back partially. The solid-liquid interface was probed through this thin liquid layer using hard X-rays (3100 eV). The sample was the working electrode in a 3-electrode cell, and it was oxidized by applying a positive potential using the potentiostat. Comparing the experimental rocking curves for Ni 3p and O 1s with theory provided thickness and roughness information for solid and liquid layers with ~1 nm resolution.

5:20pm **AS+SS-WeA10 Exploring the Usefulness of Monochromatic Ag Lα X-rays for XPS**, ***Sarah Coultas***, *J.D.P. Counsell, S.J. Hutton, A.J. Roberts, C.J. Blomfield*, Kratos Analytical Limited, UK

High energy X-ray sources have been used in XPS analysis for some time to access more core-levels and probe deeper into the sample surface. Lab

based sources such as Zr and Ti have been offered in the past but the broad X-ray line widths produced by such sources limit their applications for chemical analysis. This problem is mitigated by the use of an Ag Lα X-ray source. The source energy is 2984 eV, conveniently approximately twice that of Al Kα, hence the same quartz crystal mirror may be used to monochromate the Ag Lα X-ray line producing a narrow, high energy source of X-rays for XPS. Modern X-ray photoelectron spectrometers may be fitted with automated Al / Ag X-ray monochromators which greatly improve the usability of Ag Lα X-rays allowing Al and Ag X-ray generated spectra to be recorded from the same sample as part of automated data acquisition. Highlights of the source's characteristics include:

• Good sensitivity and energy resolution provide useful chemical information

• Enhanced surface compositional information from approximately twice the analytical depth as Al Kα radiation for same core line

• Higher excitation energy allows deeper core levels and additional Auger lines to be explored

• Large energy range of Ag Lα allows exploitation of "depth dimension" for surface segregation studies

Here we investigate the practical uses of these characteristics. This includes using the Auger parameter for aluminium and silicon containing compounds where the higher energy radiation can excite the 1s core lines and the KLL Auger series. Earlier studies [1] have shown the usefulness of higher excitation energies in elucidating structure via Auger parameters.

We also illustrate the usefulness of Ag Lα as an additional tool for the surface analyst by way of examples of spectroscopy, ARXPS, depth profiling and imaging.

1. References

[1] J.E. Castle, L.B. Hazell & RH West, *J. Electron Spectrosc. Relat. Phenom.* ., 1979, **16**, 97

5:40pm **AS+SS-WeA11 Optimizing the TOF-SIMS CsM^+ Depth Profile of a Tunnel Magneto Resistance (TMR) Structure**, ***Alan Spool***, HGST, a Western Digital Company

Used now for many years in modern magnetic recording devices, TMR sensors consist at their heart of a complicated series of layers, mostly metallic, ranging in thickness from less than a nm to several nm. In order to use the potentially better depth resolution and sensitivity of a SIMS depth profile over other surface analytical techniques, CsM^+ profiles were obtained using a variety of conditions. The ratio of the sputter ion to primary ion fluences, the sputter ion beam energy, and the % of Cs in a combined Cs/Xe sputter ion beam were all varied, and the results for a single wafer compared. In addition to changes in various CsM^+ ion intensities and therefore their signal to noise, the Cs/Xe ratio sometimes had unexpected effects on the profile shapes. The primary ion beam fluence was lessened by increasing its raster size over more than the crater bottom. Depth profiles were then created retrospectively from the raw data, using the results themselves to select the flattest portion of the crater bottom.

6:00pm **AS+SS-WeA12 Interface and Composition Analyses versus Performances: How to Improve Perovskite Solar Cells**, *Y. Busby,* University of Namur, B-5000 Namur, Belgium, *F. Matteocci,* University of Rome "Tor Vergata", Italy, *G. Divitini, S. Cacovich,* University of Cambridge, UK, *C. Ducati,* University of Cambridge, *A. di Carlo,* University of Rome "Tor Vergata", Italy, ***Jean-Jacques Pireaux***, University of Namur, Belgium

Hybrid halide perovskite solar cells (PSCs) have received much attention during the very last years because of their very promising cost/performance ratio. Different architectures and preparation methods have been tested, but still some general guidelines for their optimization are missing. In particular, the interfaces are now well known to play a dominant role in the device performances but have been so far poorly studied.

In this work, we correlated the solar cell characteristics to their interface composition and morphology in PSCs deposited by different procedures (single-step, double-step by dipping, double-step by a vacuum assisted technique) and different conversion environments (air, vacuum and nitrogen atmosphere). The interface quality is found to be affected by the perovskite conversion method and in particular from the environment where the conversion is performed. Power conversion efficiencies between 7 and 14.5% have been measured from the characteristics of the differently prepared cells. The morphology, crystal size and interdiffusion have been fully characterized by scanning transmission electron microscopy (STEM), equipped with high resolution energy-dispersive X-ray spectroscopy (EDX). Interfaces have been further characterized by depth profile techniques by combining ion beam sputtering with atomic and molecular composition analysis with X-Ray photoelectron spectroscopy (XPS) and Time of Flight Secondary Ion Mass Spectroscopy (ToF-SIMS). In particular these techniques allowed detecting and evaluating the diffusion of metals into the hole transport material (SpiroOMetAD) and iodine and chlorine diffusion in the TiO_2 back contact. Interestingly, the higher oxygen content perovskite formed in air is not associated to a sensibly lower (short term) efficiency of the solar cell.

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