

Monday Afternoon, October 20, 2008

Applied Surface Science

Room: 207 - Session AS-MoA

Electron Spectroscopies

Moderator: A. Herrera-Gomez, Cinvestav-Unidad Queretaro, Mexico

2:00pm **AS-MoA1 Probing the Interfacial Chemistry of Polymer-Metal Systems with Electron Spectroscopy**, *J.F. Watts*, University of Surrey, UK **INVITED**

The nature of the interface between a polymer phase and a metallic substrate is crucial in many important technological endeavours, for example; adhesive bonding, organic coatings for corrosion protection and sealants. XPS has been used for many years for the forensic analysis of failed interfaces, and in some cases the analysis of interfacial failure surfaces may provide a means to understanding adhesion, and perhaps even identifying certain species that are responsible for compromising performance. However in most cases it is necessary to resort to specimen preparation strategies that allow the surface chemical analysis of the necessarily thin layer responsible for adhesion between the two phases in order to investigate the interfacial chemistry of adhesion. Two methods developed in the author's laboratory, which allow access to the interfacial region, will be described. The deposition of a very thin layer ($< 2\text{nm}$) of organic material, either a component of an adhesive or coating or a dilute solution of the fully formulated system itself, provides a route to probing the interfacial chemistry directly using XPS and ToF-SIMS. The C1s XPS data provides information regarding the changes in carbon chemistry occurring at the interface and fine structure in cationic spectra provide indications of bond formation between organic layer and substrate. This may lead to the conclusion of the existence of specific interactions across the interface and the presence of these can often be confirmed with ToF-SIMS. An alternative approach is to section a polymer/metal system to expose the interface for analysis. The use of ultra-low angle microtomy (ULAM) cut at angle in the range of $0.003 - 2$ degrees relative to the interface has been shown to be extremely effective. Once prepared small area XPS can be used to profile across the interface and in the best cases a depth resolution of < 20 nm can be achieved. Using this approach it has been possible to establish the interdiffusion of active components in a paint system and the aggregation of adhesion promoter molecules, incorporated in an adhesive formulation, at the interface of aluminium bonded with a commercial epoxy adhesive.

2:40pm **AS-MoA3 2-Dimensional X-Ray Photoelectron Spectroscopy for Composite Surface Analysis**, *S. Suzer*, Bilkent University, Turkey

We describe a method for obtaining 2-Dimensional X-Ray Photoelectron Spectroscopic data derived from the frequency dependence of the XPS peaks recorded under electrical square-wave pulses, which control and affect the binding energy positions via the electrical potentials developed as a result of charging. By using the frequency dependence of the peaks and their cross-correlations, our technique enables us to elucidate electrical characteristics of surface structures of composite samples and bring out various correlations between hidden/overlapping peaks. Application of this technique to various composite surface structures will be presented, and discussed.

3:00pm **AS-MoA4 Evaluation of Uncertainties in X-ray Photoelectron Spectroscopy Intensities Associated with Different Methods and Procedures for Background Subtraction**, *C.J. Powell, J.M. Conny*, National Institute of Standards and Technology

We report uncertainties in X-ray photoelectron spectroscopy (XPS) intensities arising from commonly used methods and procedures for subtraction of the spectral background. These uncertainties were determined from a comparison of XPS intensities reported by volunteer analysts from 28 institutions and the corresponding intensities expected for a set of simulated XPS spectra. We analyzed peak intensities from 32 sets of data for a group of twelve spectra that had been simulated for a monochromatized Al K α source. Each reported intensity was compared with an expected intensity for the particular integration limits chosen by each analyst and known from the simulation design. We present ratios of the reported intensities to the expected intensities for the background-subtraction methods chosen by the analysts. These ratios were close to unity in most cases, as expected, but deviations were found in the results from some analysts, particularly if the main peak was asymmetrical or if shakeup was present. We showed that better results for the Shirley, Tougaard, and linear backgrounds were obtained when analysts determined peak

intensities over certain energy ranges or integration limits. We will present recommended integration limits for the three backgrounds that should be useful in the determination of peak intensities for other XPS spectra.

3:20pm **AS-MoA5 Investigation of Shallow Buried Interfaces by Photoelectron Spectroscopy and its Application to Protective Films on Metals**, *Y. Wang, P.M.A. Sherwood*, Oklahoma State University

It is generally very important to understand the chemical interactions that may occur at a buried interface in order to evaluate the choice of surface coatings that might be used in many practical applications. In order to make such a study it is generally possible to produce a very thin film of surface coating that is sufficiently thin to allow photoelectron spectroscopic data to be obtained from the interfacial region. The use of core and valence band photoemission to probe shallow buried interfaces will be illustrated using a number of examples of thin films on metals and carbon fibers. In particular the presentation will illustrate how thin oxide-free films of phosphate on steel surfaces can be studied, and their interaction with polymer films investigated. The effect of corrosive environments using water and saline solutions on these surfaces will be reported. It will be seen that the oxide-free phosphate films provide corrosion protection for the steel, and that the corrosion behavior is impacted by the addition of thin polymer films. The surface chemistry can be determined by using difference spectra, and by interpreting the valence band data by comparison with calculated spectra obtained from band-structure and other calculations.

4:00pm **AS-MoA7 Looking Beneath the Surface: Electron Spectroscopy with X-ray Standing Waves and Hard X-rays**, *C.S. Fadley*, University of California, Davis and Lawrence Berkeley National Laboratory **INVITED**

I will discuss two relatively new developments in photoemission: the use of nanometer-scale standing-wave (SW) excitation so as to selectively look at different depths below the surface^{1,3} and the use of harder x-ray excitation in the multi-keV range so as to probe more deeply below the surface, in what has been termed HAXPES or HXPS.⁴ Both of these approaches have the potential for enhancing the sensitivity of photoemission to both bulk and buried interface properties, while at the same time permitting the study of near-surface phenomena. After a brief overview of basic concepts, I will discuss several recent applications of these methods, separately and in concert. These will include: variable-temperature HXPS measurements at the ESRF on fractured cubic and cleaved bilayer lanthanum strontium manganite samples,^{5,6} SW HXPS measurements at both BESSY⁷ and SPring8⁸ on systems of relevance to spintronic and semiconductor IC applications, the possibility of doing angle-resolved HXPS so as to carry out band mapping,⁹ and the possible benefits of photoelectron diffraction in the hard x-ray regime for local structure determinations.¹⁰

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⁵F. Offi et al., *Phys. Rev. B* 75, 014422 (2007).

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¹⁰A. Winkelman and C.S. Fadley, to be published.

4:40pm **AS-MoA9 Methods for X-ray Photoelectron Spectromicroscopy**, *C.J. Blomfield, A.J. Roberts, S.J. Hutton*, Kratos Analytical Ltd, UK, *N. Fairley*, Casa XPS Ltd, UK

Fast parallel XPS imaging of surfaces has been commercially available for more than a decade. During this time numerous examples of both elemental and chemical state images have been published. X-ray photoelectron imaging has become a routine technique for the determination of lateral distribution of elements and chemical species at the surface and capable of a lateral resolution of $< 3\mu\text{m}$ over areas of several millimetres. More recently the spherical mirror analyser (SMA), used for energy selection in XPS imaging applications, has been combined with the delay line detector (DLD), a two-dimensional, pulse counting electron detector. This detector has allowed the realisation of quantitative surface chemical state microscopy by XPS. To generate such information requires the acquisition of a several images, or a series of images, incremented in energy so that each pixel contains photoelectron intensity information as a function of photoelectron energy. Fast counting electronics enable the detector to collect over 65,500 pixels per image. The different methods of collecting

the necessary data and the application of multivariate analysis to analyse the information content of the data and as a tool for noise reduction in individual images or spectra will be described. Methods for obtaining the maximum information from the minimum acquisition time will also be discussed. The application of the various approaches to a variety of diverse samples will be presented.

5:00pm **AS-MoA10 Structural Properties of Epitaxial SrHfO₃ Thin Films on Si(100)**, *M. Sawkar-Mathur*, University of California, Los Angeles, *C. Marchiori, J. Fompeyrine*, IBM Zurich Research Laboratory, *J. Bargar, M. Toney*, Stanford Synchrotron Radiation Laboratory, *J.P. Chang*, University of California, Los Angeles

Hafnium based amorphous oxides are currently being implemented to enable the 45-nm and 32-nm technology nodes of metal oxide semiconductor field effect transistors (MOSFETs). However, the interfacial issues arising at the amorphous oxide/crystalline Si interface justify the exploration of a lattice-matched crystalline oxide on Si to achieve an atomically sharp interface, thereby improving the device reliability. In this work, SrHfO₃, a perovskite oxide, was grown on silicon using molecular beam epitaxy (MBE). In-depth structural analysis using synchrotron techniques including XRD with a four circle diffractometer and grazing incidence EXAFS was performed to determine the crystalline quality and short range chemical bonding and order in these ultra-thin SrHfO₃ films. Nearly epitaxial growth of SrHfO₃ on Si was observed with good crystalline quality and some misalignment of grains. From the in-plane diffraction pattern, the SrHfO₃ (100) plane was found to be parallel to the Si(110) plane, yielding a 6% lattice mismatch. The d spacing of the SrHfO₃ (300) plane was found to be 1.37 Å which corresponds well with the literature reported value of 1.36 Å, suggesting no significant strain in the film. Phi scans of the SrHfO₃ (200) peak showed the four-fold symmetry expected for that plane, with no twinning, further substantiating the lack of significant strain in the film. The atomic planes were found to be highly parallel, as evidenced by the presence of interference fringes around the SrHfO₃ (001) plane. Cluster models with a radial distance of 4 Å were constructed using the perovskite crystal structure of SrHfO₃ to model the scattering amplitudes of the absorption spectra and quantify the nearest and second nearest neighbors surrounding the center absorbing Hf atom. A low level of disorder and minimal defects were observed. Based on the complementary analyses of synchrotron GI-EXAFS and XRD, MBE grown SrHfO₃ on Si has the potential to be a crystalline metal oxide for implementation in CMOS devices.

5:20pm **AS-MoA11 Improved Depth Resolution for Scanning Auger Analysis Using a Novel Sample Preparation**, *W. Liu, S. Schauer, D. Theodore, H. Ramirez*, Freescale Semiconductor Inc.

Auger depth profile analysis can be impeded by the roughening during ion sputtering. This is especially noticeable when analyzing semiconductor devices, because of the variety of materials that are susceptible to roughening, and the importance of very thin interfaces. A novel technique is presented in this paper, which combines scanning Auger analysis with FIB thinning, for analysis of single via interfacial structures in failure analysis of ICs devices. After a failing structure was identified by electrical fault isolation techniques, FIB sample preparation removes all the materials from top of the device including polyimide, passivation, metal layers, dielectric layers (ILD) until reaching about 200 Angstroms above the via interface in tungsten plug. Then a PHI SMART 200 scanning Auger instrument with a Physical Electronics model 06-350 ion gun was used for Auger depth profiling of this single via. A thin oxidized interface was observed between TiN glue layer and TiN ARC (anti-reflection coating) which resulted in the via failure. This layer would have been impossible to detect using conventional sputter depth profiling techniques. It was concluded from the following investigation and experiments that this interfacial material was caused by the "backsputtering" of ARC TiN during via etch and RF sputtering before TiN glue deposition.

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