Tuesday Morning, November 16, 2004

Applied Surface Science
Room 210A - Session AS-TuM

Electron Spectroscopies

Moderator: R. Haasch, University of Illinois, Urbana

8:20am **AS-TuM1 Light Induced Chemically Resolved Electrical Measurements (LICREM) in XPS: Anomalous Photoresponse of CdSe Nanoparticle Films***, **H. Cohen**, S. Sarkar, G. Hodes,* The Weizmann Institute of Science, Israel

A novel method, based on electrically and optically stimulated XPS, is applied to thin overlayers of CdSe nanoparticles. Negative differential resistance is observed in the dark chemically resolved electrical measurements (CREM)@super1@. The photoresponse under variable electrical conditions shows that the system can operate in two modes, differing in the direction of photocurrent. A phenomenological model is provided, explaining the anomalous photoresponse by means of competing charge trapping mechanisms, which allow real-time shaping of space charge and, hence, of the local electric fields. @FootnoteText@ @footnote 1@ H. Cohen, Condensed Matter Archive 031147, (Nov. 20, 2003).

8:40am **AS-TuM2 Validation of Information Gained from the XPS Survey Scan***, **J.E. Castle**, C. Lavie-Compin,* University of Surrey, UK

Members of the 34th IUVSTA workshop @footnote1@ reported an â?oimplementable protocol for the collection and analysis of a standard survey scan; allowing extraction of the maximum available informationâ?⍰. This information might then guide the next steps in sample analysis or might be sufficient in itself. Autonomous extraction of information required in corrosion science has been discussed @footnote2@. Here we compare data obtained from the survey scan with high resolution scans for four Cu/Ni alloys. They were examined: a) ion-etched ; b) carrying the air-formed oxide and contamination; c) after oxidation in air at 100ÂºC; and d) as c) with a brief ion-etch. The survey scan was used to determine key data including: a) testing for adventitious contamination by organic molecules @footnote3@; b) the thickness of the contamination layer; c) the apparent surface composition, corrected for the influence of contamination; d) the surface enrichment factor and enrichment rank; e) the principle chemical species in the surface, determined by the Auger parameter, and/or the presence of satellites @footnote4@; f) the thickness of the oxide, determined by peak fitting regions taken from the survey scan. The comparison enables the value of guidance given by the survey scan and the extent to which it is sufficient for purpose, to be assessed. @FootnoteText@ @footnote1@ J.E.Castle and C.J.Powell â?oReport on the 34th IUVSTA Workshop â?~XPS: from spectra to results â?" towards an expert systemâ?⍰ Surf.Interface Anal. 36 pp225 - 37 (2004) @footnote2@ J.E.Castle â?oModules for an XPS Expert System: Applications in Corrosion Scienceâ?⍰, QSA Symposium: AVS 50th Meeting, Baltimore 2003. @footnote3@ J.E.Castle and M.A.Bakerâ?oThe Feasibility of an XPS Expert System Demonstrated by A Rule Set for Carbon Contaminationâ?⍰ J. Elec Spec Related Phenomena, 105 pp245 - 256 (1999) @footnote4@ J.E.Castle â?~A Wizard Source of Expertise in XPSâ?T Surf.Interface Anal. 33 pp 196 - 202 (2002).

9:00am **AS-TuM3 Extensions of Photoelectron Spectroscopy to the Study of Nanoscale Systems***, **R.L. Opila**, K. Demirkan, A. Mathew,* University of Delaware **INVITED**

Photoelectron spectroscopy (PES) is a very powerful probe of elemental composition and structure at nanometer length scales. PES of core levels can identify which atoms are present, their relative concentrations, and their chemical bonding. PES of the valence levels yields more insight into the chemical bonding. This technique achieves its surface sensitivity from the charge on the photoelectron and its high probability of inelastic collisions. This complication provides both complications and opportunities. First, the photoelectrons are not collected as a linear function of depth, but approximately by an exponentially decreasing function of depth, where the decay length is given by an average of the emission depth distribution function. Collecting the emitted photoelectrons over several angles changes the sampled range of depths. Several algorithms have been proposed that permit the variation in intensity as a function of collection angle to be converted to elemental concentration as a function of depth. We will discuss a maximum entropy algorithm and show its application to study of high-k dielectrics as gate oxides for transistors. The charge on the photoelectrons also samples the local electronic charges that might be present. Through Coulombic interaction with these charges, their kinetic energy is shifted. It is possible to determine the amount of fixed charge present at a chemical interface by determining the relative shift between the photoelectrons emitted from overlayer and those from the substrate. Examples of interfacial charge, including high-k oxide/Si and Al2O3/Al, will be discussed.

9:40am **AS-TuM5 XPS Chemical Depth Profiling Using C@sub 60@ Ion Beams***, **N. Sanada**, A. Yamamoto, H. Iwai,* ULVAC-PHI, Inc., Japan*; J.F. Moulder,* Physical Electronics*; R. Oiwa, Y. Ohashi,* ULVAC-PHI, Inc., Japan

XPS is one of the most common analytical techniques which can be applied to the chemical analysis of a wide range of materials such as organic polymers, ceramics, metals and semiconductors. However, depth profiling with XPS requires sputtering with ion beams, which are well known to induce sample damage and have the constraint of sample chemical information being lost. Recently, we have applied a buckminsterfullerene (C@sub 60@) ion beam for depth profiling during XPS analysis[1]. A practical sputter rate of 2.4 nm / min. for SiO@sub 2@ was obtained with a sputtered area of 5 mm x 5 mm using a 5 kV C@sub 60@ ion beam. Extremely low sputtering degradation of organic polymers such as polytetrafluoroethylene[1], a polyester, a gelatin, and a latex [2] were observed under these conditions. In the meantime, the carbon contaminants derived from the C@sub 60@ ion beam varied under different sputter conditions. We studied the beam condition using a thermally oxidized SiO@sub 2@ film sample to minimize carbon residue determined by XPS. The quantities of carbon residue in the SiO@sub 2@ film reduced from 85 at% to 0.2 at% as the beam energies were modified from 2 keV to 30 keV. The incidence angle of the ion beam also affected the carbon residue in the film. XPS chemical depth profiling with C@sub 60@ sputtering applied to organic thin films will be discussed in this presentation. [1] N. Sanada et al., Surf. Interf. Anal., 36, 280 (2004). [2] N. Sanada et al., Extended Abstracts 51st Spring Meeting, 2004; Jpn. Soc. Appl. Phys. Rel. Soc. 29p-YD2.

10:00am **AS-TuM6 X-Ray Photoelectron Spectroscopy of Rubber Compounds: Temperature Dependence and Crosslink Distribution***, **G.E. Hammer**,* The Goodyear Tire & Rubber Company

Rubber compounds are complex mixtures of ingredients, including many mobile and volatile species. Exposure to the ultra high vacuum environment common to surface analytical instruments can therefore cause significant changes in a rubber surface and produce misleading and even erroneous results. In this work it has been shown that stable, representative x-ray photoelectron spectra could be obtained if the specimen was pre-cooled below a compound-dependent maximum temperature before exposure to the vacuum environment. Maximum temperatures were found to be -50°C and -70°C for two typical tire rubber compounds, a wire adhesion formulation and passenger tire tread, respectively. Effects of specimen preparation were further investigated. High resolution x-ray photoelectron spectra of specimens pre-cooled to -85°C and analyzed at -140°C indicated a correlation between the sulfur peak positions and the length of sulfur crosslinks in the rubber. Specifically, a linear relationship was found between sulfur 2p binding energy and the percentage of polysulfide crosslinks as determined by standard bulk solvent swelling analysis for three different rubber compounds based on two different polymers.

10:20am **AS-TuM7 Monte Carlo Simulations of Electron Backscattering from Surfaces in Scanning Auger Microscopy***, **C. Powell**,* NIST*; A. Jablonski,* Institute of Physical Chemistry, Poland

Monte Carlo (MC) simulations are useful for calculating signal intensities in AES because multiple-scattering events can be conveniently included. In this contribution, a new MC algorithm for AES is presented in which recent advances in knowledge of electron transport are incorporated. Differential cross sections for elastic scattering were obtained from a NIST database.@footnote 1@ The inelastic-scattering events were described by energy-loss functions derived from optical data, and "recommended" inelastic mean free paths for energies up to 10 keV were utilized.@footnote 2@ The empirical formula of Casnati et al.@footnote 3@ was used to describe inner-shell ionization cross sections. Particular care was taken in preparing the random number generators for simulation of the angular and energy distributions after elastic- and inelastic-scattering events because of numerous sharp features (e.g., deep minima) in the relevant probability distributions. We report new calculations of the backscattering factor (BF) for Auger transitions of Si, Cu, Ag, and Au as a function of primary energy, and find that the BF depends also on the Auger-electron emission angle. We investigated the radial distribution of emitted Auger electrons from a thin Cu film on Si and Au substrates. Due to the effects of electron backscattering, the radius of the analysis area depends considerably on the primary energy and the substrate, and can be much larger than the radius of the primary beam. We also examined the effects of backscattering on Auger line scans in the vicinity of the edge of a Cu film on Si and Au substrates. @FootnoteText@ @footnote 1@A. Jablonski, F. Salvat, and C. J. Powell, NIST Electron Elastic-Scattering Cross-Section Database, Version 3.1, SRD Database 64 (2003). @footnote 2@C. J. Powell and A. Jablonski, J. Phys. Chem. Ref. Data 28 (1999) 19. @footnote 3@E. Casnati, A. Tartari and C. Baraldi, J. Phys. B 15 (1982) 155.

10:40am **AS-TuM8 Round Robin Study of Evaluation of Electron Beam Damage of SiO2/Si in Auger Microprobe Analysis*, S. Tanuma,* *T. Kimura,* National Institute for Materials Science (NIMS), Japan*; S. Hashimoto,* Kokankeisoku, Japan*; M. Inoue,* Setsunan University, Japan*; M. Suzuki,* ULVAC-PHI, Inc., Japan

Auger electron spectroscopy (AES) is routinely employed for characterization of wafers at various stages of device fabrication, for the identification of defects, and for process development. A major limitation of AES, however, is the fact that the incident electron beam can initiate unwanted chemical changes. While many investigations have been made on electron irradiation damage of silicon dioxide during analyses by Auger electron spectroscopy (AES), it is very complicated or tedious to determine the critical dose for such damage from intensity changes of the silicon L3VV Auger spectrum versus irradiation time. Then, we plan to make an accurate and quantitative method of the evaluation of surface damage on the specimen caused by the electron beam irradiation. We have made measurements of the Si L3VV spectrum on SiO2 (100nm)/Si and SiO2 (10nm)/Si specimens versus electron dose at 3, 5, 10 and 15 keV. The measurements were carried out for a wide range of the total irradiation dose: 0.001 - 150 C/cm2. We found that the peaks to background intensities of Si LVV metallic peaks are changed due to the increase of measurement time (or total electron dose). We have also developed an equation that represents the Si LVV metallic peak intensities as a function of total electron dose, based on the two-step decomposition model for SiO2. This method has two parameters that represent the EDCS of SiO2 and SiO, respectively. Form the curve fit of the proposed equation to the measured Si LVV metallic peak intensities, we can determine the critical dose of electrons for SiO2 decomposition quantitatively.

11:00am **AS-TuM9 Performance of a High throughput TOF-HREELS Analyzer*, Z. Yang,*** University of Maine*; R.H. Jackson,* Stillwater Scientific Instruments*; P.H. Kleban, B.G. Frederick,* University of Maine

Despite tremendous advances in monochromators, the efficiency of conventional analyzers in high resolution electron energy loss spectrometers (HREELS) is poor (~ 0.1%) due to the serial nature of the dispersive analyzer: only 1 out of typically 2000 energy channels can be measured at any one time. Pseudo-random binary sequence modulation is a method of multiplexing in the time domain to increase the throughput of the analyzer to 50%. We have combined PRBS modulation in an electron time-of-flight analyzer with maximum likelihood signal recovery methods to decrease data acquisition times from hours per spectrum to a few minutes, while maintaining resolution in the 2-4 meV range. We will present results from several samples that demonstrate the capabilities of the state-of-the-art time-of-flight TOF-HREELS instrument. Data measured on azimuthally oriented polytetrafluoroethylene (Teflon) films reproduce the complex spectral features and achieve resolution comparable to spectra measured with the conventional instrument. Results on the c(2x4) O/Pd(110) surface, in which the intensity of the oxygen-metal stretch relative to the elastic peak is < 0.1%, demonstrates the large dynamic range that has been achieved, again with resolution below 3 meV off the surface. Similar performance is obtained for CO/Pd(110), in good agreement with recently published spectra by Kato, et al.@footnote 1@. @FootnoteText@ @footnote 1@ Kato, H.; Okuyama, H.; Ichihara, S.; Kawai, M.; Yoshinobu, J. J. Chem Phys 2000, 112, 1925.

11:20am **AS-TuM10 Oxygen Environmental Electron Spectroscopy and Microscopy: A New Concept for Reducing Harmful Electron Beam Effects on Insulating Samples*, Y. Ji,*** *H. Guo,* Beijing University of Technology, China*; V. Kempter,* Technische Unviversität Clausthal, Germany

Charging phenomena occur on insulating surfaces in many types of surface analysis techniques. In the case of electron spectroscopy and microscopy using an electron beam as probe, the charging phenomena can seriously distort the spectra and images, even make the analysis impossible. In addition, the electron beam can change the surface composition through electron stimulated desorption (ESD) and electron stimulated adsorption (ESA). These effects on oxide samples in Auger electron spectroscopy analysis can be markedly reduced or eliminated in oxygen pressures @<=@ 6*10@super -@@super 6@ Pa. Using oxygen environment to reduce the surface charging-up is based on a novel concept: Reducing the charging effects through eliminating electron traps resulting from electron beam damage, specifically, the ESD of surface oxygen. This is a breakthrough in the understanding of the charging mechanism, as the existing methods for reducing charging-up are mostly based on considerations such as increasing the surface conductivity by coating a conducting layer, increasing the secondary electron yield by applying an additional low energy electron beam, neutralizing the negative surface charges by providing positive charges, increasing the bulk conductivity by sample heating, etc. The significance of this method is that it can also compensate the depletion of the surface oxygen due to ESD and eliminate the surface contamination from background adsorption; it is applicable to other analysis techniques such as scanning electron microscopy, electron probe microanalysis, electron diffraction, electron energy loss spectroscopy.

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