

Monday Afternoon, October 31, 2005

Applied Surface Science

Room 206 - Session AS-MoA

Electron Spectroscopies

Moderator: R.L. Opila, University of Delaware

2:00pm AS-MoA1 High Resolution XPS and EELS of Assembled Organic Monolayers, *J.-J. Pireaux*, University of Namur, Belgium **INVITED**

Everyday application of XPS allows to unravel with quite simple procedures the elemental and chemical composition of materials surface in a quantitative way. Core and valence band spectra analyses do contain structural information as well : to gather it, high resolution analysis and sometimes study of reference materials are necessary. This will be demonstrated with the determination of the good-or-bad assembling property of some silane molecules with different hydrocarbon chain length deposited from a solution onto TiO₂ single crystals ; a model of the -Si-O-Ti-O- interfacial layer will be presented. While XPS and UPS synchrotron photoemission valence band analysis remain still qualitative for the determination of structural order, we will show that high resolution electron energy loss spectroscopy (HR)EELS can be successfully used to evaluate the crystalline domain size of alkane thiols layers assembled on gold surfaces ; indeed, the measure of the angular distribution of the scattered electrons corresponds to a diffraction experiment. With contributions of R. Magnée, Ch. Grégoire and A.-S. Duwez

2:40pm AS-MoA3 Evaluation of Electron Back-scattering in Auger Analysis using a Cross-sectioned GaAs/AlAs Superlattice, *M. Suzuki, N. Urushihara, S. Iida, N. Sanada*, ULVAC-PHI, Inc., Japan; *D.F. Paul, J.S. Hammond*, Physical Electronics; *A. Yamamoto*, ULVAC-PHI, Inc., Japan

It is generally well known that when using electron excitation analysis techniques such as Auger electron spectroscopy, the analyzed volume is expanded due to the scattering effects in a solid surface region. We will present experimental results to evaluate generation of Auger electrons by inelastic scattered electrons. A cleaved cross-section of a GaAs/AlAs superlattice, consisting of three different thicknesses of repeating layers of GaAs/AlAs (50 nm/50 nm, 20 nm/20 nm, and 10 nm/10 nm) was analyzed with a scanning Auger Nanoprobe. Along the analyzed line perpendicular to the 50 nm thick-layers, the kinetic energy of the Al KLL Auger electrons varied by 5 eV to 6 eV, with a spatial distribution corresponding with the GaAs/AlAs superlattice structure. The amplitude of the Auger peak energy shift with beam position was smaller for the 20 nm-thick layers and almost negligible for the 10 nm-thick layers. The highest and lowest Auger energy positions correspond to the AlAs and GaAs layers, respectively. The analyzed surface was covered with a naturally oxidized layer, as the cleavage was carried out in air. The lower Al kinetic energy signal was detected when the electron beam hit the AlAs region, due to the reduction of aluminum oxide caused by electron beam. The higher Al kinetic energy signal associated with aluminum oxide was generated by inelastically scattered electrons when the beam was at the GaAs region. These results will be discussed based on a model of electron scattering. @FootnoteText@ @footnote1@ M. Arai et al., O-32, The third international symposium on practical surface analysis (PSA-03), Korea, October 2003.

3:00pm AS-MoA4 Angle Resolved XPS for Characterization and Metrology of Ultra-Thin Silicon Oxynitride Films, *C.R. Brundle*, C. R. Brundle & Associates; *G. Conti, Y. Uritsky*, Applied Materials, Inc.; *P. Mack*, Thermo Electron Inc., UK

The analytical tool set used in the wafer processing industry for metrology of thin films is changing because the films are becoming so thin and more complex. One of the new contenders for both characterization (the kind of detailed information needed in development, trouble shooting, and failure analysis) and metrology (rapid measurements of specific parameters on large numbers of samples) is XPS. Whereas many of the techniques used in the past become less effective as films become ultra-thin (0 to 50Å range), XPS becomes most effective in this range. For the high k dielectric material, SiON, as used in the current generation of gate oxide production (10 to 30Å), Angle Resolved XPS can provide very precise film thickness and at the same time, in principle, provide a depth distribution of the nitrogen dose using a constrained model to fit the data. Since the model fit to the data can never be unique the approach works best for two extremes: 1) when there are really gross differences in distributions between films and it is this qualitative difference one is looking for and 2) when there are multiple measurements available for films made under a given processing condition that give the same profile fit, and then multiple measurements under a different processing condition which give a consistently different fit (even if

small), signifying that a change in profile has occurred. We present examples of both situations from current industry samples. The former is more of a film/process development issue and the latter is more of a metrology issue. It does seem possible to tell that small changes in distribution have occurred, even if one cannot fully quantify those changes. An interesting point is that in none of the many (hundreds)of samples studied, is a spike in the N concentration observed at the surface (first 2Å) by ARXPS, unlike in some reports using TOF-SIMS on similar samples.

3:20pm AS-MoA5 Multi-Technique Characterization of Iron Nanoparticles, *D.R. Baer, M.H. Engelhard, C.M. Wang, K.H. Pecher*, Pacific Northwest National Laboratory; *R.L. Penn*, University of Minnesota; *P.G. Tratnyek*, Oregon Health and Sciences University; *Y. Qiang*, University of Idaho; *D.E. McCready, J.C. Linehan, J.E. Amonette*, Pacific Northwest National Laboratory; *J. Antony*, University of Idaho

Understanding the chemical properties of iron nanoparticles requires detailed information about the size, physical and chemical structure and the presence of surface coatings. Because of the reactive nature of iron, these particles are usually covered by some type of incidental or deliberately added protective layer. In spite of any protection, the properties of the particles change with time and are altered by the environments they have been exposed to and in some cases by the manner the samples have been handled prior to analysis. For some of our reaction studies, we expect the particles to react and change with time and it is important to understand this particle evolution. This presentation will describe aspects of nanoparticle synthesis and processing, the methods we are using to handle the samples, the priority and order of the analysis, and the information we expect from each method. Methods routinely used include: x-ray photoelectron spectroscopy; transmission electron spectroscopy; x-ray diffraction; surface area analysis; x-ray adsorption spectroscopy. These are correlated with measurements of electrochemical properties and chemical properties. The issues and challenges of forming a consistent picture of the particles as a function of time will be discussed.

3:40pm AS-MoA6 Workfunction Differences between Cu Grains: Laterally Resolved UPS with the NanoESCA, *J. Westermann, D. Funnemann, B. Kroemker*, Omicron NanoTechnology GmbH, Germany

Recently, we have developed an imaging XPS spectrometer with lateral resolution in the range of 200nm and below. This instrument has recently been used for the study of work function differences on a variety of samples. Main focus of this application was the work function variation between different copper grains. As copper is currently of great interest as a material for interconnects in semiconductor devices, the understanding of grain properties is a key for the improvement of the interconnect properties. Samples were provided by the Laboratoire d'Electronique de Technologie de l'Information (LETI, Grenoble). Using the NanoESCA, we can show for the first time the relation between secondary electron intensity and work function with a high spatial resolution. Surprisingly, this does not follow the Fowler plot as was expected previously. In addition, we show measurements on a heterogenous material combination with microstructured Gold patterns on a Silicon Oxide sample. These data demonstrate the powerful combination of imaging with spectroscopy: We identify regions of band-bending, charging and different work-functions. @FootnoteText@ @footnote 1@ Escher et al., J.Phys.:Condens. Matt 17 (2005) 1329-1338@footnote 2@ Escher et al., J. Electron Spectrosc. Relat. Phenom., 144-147 (2005) 1179-1182@footnote 3@ Przychowski et al., Surf. Sci. 549 (2004) 37-51.

4:00pm AS-MoA7 In-Situ and Ex-Situ Characterization of the Electrochemically-Accelerated Corrosion of Ni-Cr-Mo-Gd Alloy Surfaces in Aqueous Media, *P.J. Pinhero, T.E. Lister, R.E. Mizia, T.L. Trowbridge*, Idaho National Laboratory; *A.W. Glenn*, Idaho Completion Project

A new thermal-neutron-absorbing structural Ni-Cr-Mo-Gd alloy was developed at the Idaho National Laboratory (INL). The purpose of this alloy is to potentially absorb neutrons liberated from spent nuclear fuel (SNF) and mitigate any issues related to nuclear criticality. The microstructure of this alloy indicates a two-phase structure consisting of the primary Ni-Cr-Mo austenite matrix phase and secondary Ni@sub 5@Gd phase inclusions arising from the precipitation of the austenite-insoluble Gd. Presently, this alloy is under consideration for use within the U.S. Department of Energy (DOE) standardized SNF waste packages. To support the case for this alloy's acceptance and understand its more fundamental surface character, studies were undertaken to examine its structure and composition with respect to its bulk properties, the role of oxidation and resulting passivation on its susceptibility to corrode, and finally how these properties are influenced through boron-doping. This paper focuses on the

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susceptibility of the Ni-Cr-Mo-Gd surface to corrode. Scanning electrochemical microscopy (SECM) was used to examine localized corrosion of the surface in situ. It was observed that the corrosion initiates at the interfaces between the Ni@sub 5@Gd particles and the surrounding austenite matrix. Corrosion then propagates such that these particles completely dissolve, leaving an intact "passive" Ni-Cr-Mo surface. Current-sensing atomic force microscopy (CS-AFM) images help support the argument of electron transfer initiating at the interface formed between the included particles and the austenite matrix. Ex situ analysis using focused ion beam / scanning electron microscopy (FIB/SEM), scanning Auger microscopy (SAM), and x-ray photoelectron microscopy show how the structure and surface composition change as a function of the electrochemically driven corrosion process.

4:20pm AS-MoA8 Throughput Advantages of PRBS Modulation in TOF Electron Spectroscopy and Mass Spectrometry, R.H. Jackson, Stillwater Scientific Instruments; Z. Yang, Univ. of Maine; L.J. LeGore, B.G. Frederick, P.H. Kleban, C.B.H. Crothers, D.P. Martin, Stillwater Scientific Instruments

Pseudo-random binary sequence (PRBS) modulation is a method of multiplexing in the time domain to increase the time domain efficiency of an analyzer. We have combined PRBS modulation in a time-of-flight velocity analyzer with maximum likelihood signal recovery methods in both high resolution electron energy loss spectroscopy (HREELS) and mass spectrometry (MS). In previous TOF-HREELS measurements, we have decreased data acquisition times from hours per spectrum to a few minutes, while maintaining resolution in the 2-4 meV range. Although time-of-flight instruments typically trade improvements in time domain throughput for decreases in the etendue, the use of a Bradbury-Nielsen gate chopper allows our optical design to maintain large acceptance angles from the source while achieving high throughput and resolution. We characterize the throughput advantages of a broadband input lens for use in the TOF-HREELS analyzer. Similar advantages are achieved in our GC/MS implementation of a TOF mass spectrometer, compared to the state-of-the-art orthogonal acceleration TOF-MS configuration. We also report order of magnitude improvements in the time resolution and throughput of the timing and control electronics and computational capabilities for implementation of the data recovery algorithms.

4:40pm AS-MoA9 Novel Field Emission Source for Electron Microscopy, J.W. Lewellen, J.R. Noonan, Argonne National Laboratory

A novel field emission electron source that combines desirable features of thermionic cathode and photocathode has been designed. Simulations indicate that the electron beam has very small emittance, ~ 2 nm-radian, and high average current. The emittance can be reduced to less than 0.01 nm-radian by taking beam slices, which also reduces the beam current. The source uses high gradient radio frequency (RF) fields to extract electrons off of a field emitter tip and accelerate these electrons to ~ 1.5 MeV energy. The resulting gun design show promise in a number accelerator and non-accelerator applications, such as energy recovery LINACS, TeraHertz radiation sources, high voltage electron microscopy, electron beam welding, and thin film deposition. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under contract No. W-31-109-ENG-38.

5:00pm AS-MoA10 Differential Charging of Nanoparticles on Oxide Surfaces as Determined by XPS with External Stimuli, U.K. Demirok, I. Tunc, S. Suzer, Bilkent University, Turkey

By recording the XPS spectra while applying external d.c. and/or pulsed voltage stimuli, it is possible to control the differential charging, and extract information related with dielectric properties of various surface structures. We have carried out a number of experiments to determine the charging/discharging behavior of various surface structures consisting of Au, Ag, and Pt (metallic), Titania (semiconductor), and Silica (dielectric) both as they are and also as Core-Shell type Nanoparticles using XPS with external voltage stimuli. Differences and similarities of these structures with respect to their chemical compositions, and also with respect to the form (d.c., pulsed, etc.) of the voltage stimuli applied, will be presented and discussed in detail.

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