

Thursday Morning, November 6, 2003

Applied Surface Science

Room 324/325 - Session AS-ThM

Electron Spectroscopy

Moderator: B.R. Rogers, Vanderbilt University

8:20am **AS-ThM1 Role of Vacuum Technology and Other Drivers in the Development of Surface Analysis**, *C.J. Powell*, National Institute of Standards and Technology

INVITED

A perspective will be given on the development and use of surface analysis, primarily by AES and XPS, for solving scientific and technological problems. Some of the early approaches for AES and XPS analyses will be described together with major developments (e.g., the availability of demountable flanges and suitable pressure gauges) in instrumental capabilities. Information will be presented on growth and trends in instrumental measurements with reduced uncertainties, knowledge of surface sensitivity, and knowledge and effects of sample morphology. Finally, an overview will be given of analytical resources now available for AES, XPS, and SIMS.

9:00am **AS-ThM3 Valence-band X-ray Photoelectron Spectroscopic Studies of Phosphorus Oxides and Phosphates**, *K.J. Gaskell, M.M. Smith, P.M.A. Sherwood*, Kansas State University

Valence band X-ray photoemission can be used to identify subtle chemical differences in surface chemistry. Phosphorus oxides are known in a number of different crystalline forms, and a very large number of phosphates are known some of which contain one phosphorus atom, and others contain condensed phosphates with a number of phosphorus atoms in chains, rings and three dimensional structures. The phosphorus oxides can be distinguished from the many phosphate species by valence band X-ray photoelectron spectroscopy (XPS), which is also able to distinguish between different crystalline forms of the oxides. The paper will give an overview of the phosphorus/oxygen valence band spectra, with the spectra interpreted by spectra predicted by band structure and cluster calculations. The paper will also describe how oxide free thin (less than 100@Ao@) films of phosphate species can be formed on metal surfaces, with the phosphate composition altered by changing the pH of the solution used to generate the films, and by changing the type of phosphorus acid used. The work provides an example of how valence band XPS can be especially valuable in the characterization of surface films when it is important to identify small chemical differences. This material was based upon work supported by the National Science Foundation under Grant No. CHE-0137502.

9:20am **AS-ThM4 Application of Electron Based Spectroscopies Combined with Chemical Derivatization for the Characterization of Black Carbon Surfaces**, *L.A. Langley, T.H. Nguyen, W.P. Ball, D.H. Fairbrother*, Johns Hopkins University

Black carbon (BC) is derived from charred plant materials and soot from combustion processes and is ubiquitous in the environment. It is now recognized that remarkably small concentrations of BC can have strong effects on the sorption of hydrophobic organic chemicals (HOCs). Despite the ubiquity of such BC particulates and the importance of sorption to contaminant fate and treatment, little is known about the physical and chemical variability of BC materials or the manner in which their properties can impact the sorption of HOCs in aquatic environments. The surfaces of soots and chars are best described as extended graphene sheets decorated at the edges by various surface oxides. The nature and composition of these surface oxides is believed to play a critical role in determining the sorption properties of BCs towards HOCs. Although X-ray Photoelectron Spectroscopy (XPS) can provide information on the elemental composition of the surface and detect changes in the O/C ratio of different BCs, quantification of the distribution of surface oxides by analysis of the C(1s) and O(1s) lineshapes alone is very difficult. To circumvent this problem XPS augmented by chemical derivatization has been employed in order to provide quantitative information on the distribution of oxide functional groups on the surface of BC. We will also present results on the potential application of bromine as a chemical derivatizing agent capable of titrating the degree of aromatic character in BCs. Additionally, synthetic chars generated from the pyrolysis of wood samples will be characterized as a function of their formation conditions. Results from XPS and chemical derivatization studies of natural chars and synthetic chars will be presented. These results are complemented by sorption studies, where different trends in sorption can be rationalized based on the surface characterization of the BC sorbents.

9:40am **AS-ThM5 Comparison of X-ray and Electron Beam Induced Damage Rates**, *A.S. Lea, M.H. Engelhard, D.R. Baer*, Pacific Northwest National Laboratory

While many people are aware of the effects of damaging electrons during Auger electron spectroscopy or electron microscopy, x-ray induced changes in specimens frequently occur and may be more common than often recognized or noted in the literature. Although electrons interact strongly with samples with a high damage cross-section and x-rays of similar energies interact less strongly and penetrate deeper into a material, the mechanisms of damage are often very similar. In an effort to efficiently take advantage of the variety of damage rates reported in the literature to obtain estimates for possible thresholds for different system, we have examined the rates of both electron induced and x-ray induced damage for a variety of materials. Based on the data, an approach is developed to compare x-ray damage rates reported for different systems and an approximate method for comparing electron beam and x-ray damage is reported. The electron beam damage is done using a 10 kV electron beam in a Phi 680 system while the x-ray damage is done in a Phi Quantum 2000. For at least some materials (e.g., poly(vinyl chloride) and poly(acrylonitrile)), the ratio of electron and x-ray damage rates are essentially identical even when the absolute rates differ by a factor of 10.

10:00am **AS-ThM6 Charge Referencing in XPS Analysis of Self-assembled Nano-phase Particle (SNAP) Surface Treatments**, *L.S. Kasten*, University of Dayton Research Institute; *V.N. Balbyshchev*, Universal Technology Corporation; *M.S. Donley*, Air Force Research Laboratory (AFRL/MLBT)

To investigate the surface chemistry of Self-assembled Nano-phase Particle (SNAP) SNAP films, X-ray photoelectron spectroscopy (XPS) was utilized to obtain detailed chemical state information on the coating constituents. SNAP coatings were created by forming nanosized siloxane structures comprised of hydrolyzed tetramethoxysilane (TMOS) and glycidoxypropyltrimethoxysilane (GPTMS) in aqueous solution and then crosslinking them upon application to form thin, dense protective organic surface treatment coatings on Al aerospace alloys. A charge referencing method from which accurate and reliable photoelectron peak binding energies could be determined was developed. In order to gain further insight into the chemical composition of the SNAP coatings, data from three related research efforts involving TOF-SIMS analysis of SNAP coatings, studies of the SNAP solution chemistry, and studies involving modeling of the SNAP oligomer formation process enabled some key assumptions to be made about the structure of the SNAP coatings. Based on these studies, an internal standard was chosen which enabled the spectra to be charge referenced, and the referenced data allowed accurate identification of chemical bonding states in the SNAP coatings. Results show that the Si bonds present in the SNAP film are a combination of the bonds in the individual precursors TMOS and GPTMS. The SNAP coatings retain the siloxane character of the of the GPTMS and TMOS precursors. These data support the concept that the nanosized siloxane macromolecules are retained through the coating application process and comprise the film. This was further verified by the use of a silicon chemical state plot, including the use of the modified Auger parameter. The SNAP film's Auger parameter value fell between the precursors' Auger parameter values. These surface analytical data are both self-consistent and consistent with the observations and assumptions of the model.

10:20am **AS-ThM7 Quantitative Depth Profiling of Silicon Oxynitride Films by Electron Spectroscopy**, *P. Mrozek, D.F. Allgeyer, B. Carlson*, Micron Technology Inc.

Detailed surface analysis was performed using X-ray photoelectron spectroscopy (XPS) and X-ray-induced Auger electron spectroscopy (XAES) on silicon oxynitride (SiON) films grown on silicon (Si). Results of conventional XPS depth profiling of SiON at shallow angles demonstrated high depth resolution with fine details of N and O distributions. Si Auger parameter analysis supplemented XPS by showing the extent of nitridization as a function of depth. Angle-resolved data were analyzed using QUASES-ARXPS software. Results are discussed in terms of possible growth mechanisms of SiON.

10:40am **AS-ThM8 Characterization of Silicon-Oxynitride Dielectric Thin Films using Grazing Incidence X-Ray Photoelectron Spectroscopy**, *E. Landree, T. Jach*, National Institute of Standards and Technology

The evolution of gate dielectric film thickness outlined in the 2002 International Technology Roadmap for Semiconductors (ITRS) is continually driving the need for new techniques sensitive to variations in spatial composition and thickness on the order of sub-nanometers. One of the promising techniques for characterizing ultrathin films is grazing incidence

Thursday Morning, November 6, 2003

x-ray photoelectron spectroscopy (GIXPS).@footnote 1@ GIXPS utilizes the dependence on the material properties of the film, and the incident angle of the x-rays to control the electric field penetration in the sample. Varying the angle of incidence from zero to some value slightly greater than the angle for total x-ray external reflection, it is possible to probe nondestructively the chemical nature of the film at different depths. Physical properties such as depth profile, density and thickness, are extracted by comparing the calculated photoemission spectrum of a constructing model of the film structure and the measured angle dependent photoemission spectrum. The measured dielectric thin film thickness and chemical depth profile from a diverse group of silicon oxynitride samples in the range of 2 - 5 nm will be discussed. In addition, challenges associated with the dependence of the technique upon various fundamental materials parameters will be addressed. @FootnoteText@ @footnote 1@ T. Jach and E. Landree. Journal of Surface Analysis. 9, 3 (2002).

11:00am **AS-ThM9 XPS Study of Ultrathin Ferroelectric Films, L. Vanzetti, M. Bersani, M. Barozzi, M. Anderle, ITC-irst, Italy; V. Nagarajan, T. Zhao, R. Ramesh, University of Maryland**

Lead zirconate titanate (PZT) thin films have been extensively studied for potential application in nonvolatile memory devices, infrared sensors, and microelectromechanical systems. In addition to compositional and structural factors, the impact of the thickness of the ferroelectric layer, and the interface quality have to be considered in understanding the structure-property relationship in PZT thin films. In this work we show results of our investigation on ultrathin ferroelectric films by XPS and SIMS. PbZr@sub 0.2@Ti@sub 0.8@O@sub 3@ films of varying thickness were deposited by pulsed laser deposition on SrRuO@sub 3@ buffered SrTiO@sub 3@ substrates. Ferroelectric measurements show that the switchable polarization drastically decreased as the PZT thickness is scaled down from 15 to 4 nm. XPS measurements on the two representative samples, 4 and 15nm thick, show that the composition of both films is the same. Moreover, the surface does not show ruthenium segregation from the buffer layer. This result proves that the drop in the polarization is not due to a change in the film composition. In addition, we also show SIMS depth profiling for both films.

11:20am **AS-ThM10 Auger Spectra Line Shape Study in Iron-Aluminum-Oxygen Reaction System, S. Nayak, University of Tennessee, Knoxville; H.M. Meyer, III, Oak Ridge National Laboratory; N.B. Dahotre, University of Tennessee, Knoxville**

Normalized intensity-kinetic energy Auger electron spectra were collected for different state of iron and aluminum. The standards and the samples were ion-sputtered and monitored until they attained a stable spectrum. The line-shape of spectra corresponding to iron in standard pure iron, iron oxides (FeO, Fe@sub 2@O@sub 3@ and Fe@sub 3@O@sub 4@) and Fe@sub 3@Al were compared. The spectra non-metallic irons exhibit distinctly different line shape than that of metallic iron. This change in line shape was also accompanied by shift in peak. Similarly, spectra corresponding to aluminum were collected for pure aluminum, Al@sub 2@O@sub 3@ and Fe@sub 3@Al. There is a distinct change in shape of line both in the case of aluminum and iron. The information was used to study the non-equilibrium two phenomena: (1) laser-induced reaction coating of iron oxide on aluminum alloys and (2) mechanical alloying of iron oxides and aluminum. In laser coating, the high rate of heating and cooling freeze-in the reaction between iron oxides and aluminum. Elemental mapping using the shift in peak position provides information about reaction mechanism. The spectra obtained from laser coating sample has a shape intermediate between purely metallic and oxidized iron and aluminum. The mechanically alloyed powder exhibited spectra line-shape commensurate with the extent of reaction. By choosing the window of kinetic energy, it was possible to map Fe and Al in combined and metallic state distinctly. Al@sub 2@O@sub 3@ and Fe@sub 3@Al were formed during the reaction between iron oxide and Al. The intermediate (frozen-in) reaction products showed gradual change of peak position and line shape from metallic to oxidized state for Fe and Al. The concept of line shape and peak shift was used to successfully study the reaction and its mechanism.

11:40am **AS-ThM11 The Dispersion of Quantum Well States in Cu/Co/Cu(001), Y.Z. Wu, C. Won, University of California, Berkeley; E. Rotenberg, Lawrence Berkeley National Laboratory; H.W. Zhao, University of California, Berkeley; N.V. Smith, Lawrence Berkeley National Laboratory; Z.Q. Qiu, University of California, Berkeley**

Electrons inside a metallic thin film experience confinement in the normal direction of the film to form quantum well states (QWS) which plays a key

role in a number of important properties in metallic thin films such as the oscillatory interlayer coupling, the magnetic anisotropy, the stability of magic thickness, etc. We will report the QWS study using angle resolved photoemission spectroscopy (ARPES) for Cu/Co/Cu(100) system. QWS in the normal direction were studied for both the lower and upper bands relative to the vacuum level. The QWS in both bands can be described as a whole by the phase accumulation method (PAM). The phase shift at the interface can be obtained experimentally. The experimental value of the phase shift deviates away from the value calculated by PAM. The dispersion of QWS with different in-plane momentum was studied near the normal direction. We found that the QWS dispersion depends on the Cu film thickness \propto and that the quantized perpendicular momentum changes with the in-plane momentum. The latter has a dramatic effect in obtaining the in-plane effective mass of the electron. The in-plane effective mass of Cu increases with the energy.

Author Index

Bold page numbers indicate presenter

— A —

Allgeyer, D.F.: AS-ThM7, **1**
Anderle, M.: AS-ThM9, **2**

— B —

Baer, D.R.: AS-ThM5, **1**
Balbyshev, V.N.: AS-ThM6, **1**
Ball, W.P.: AS-ThM4, **1**
Barozzi, M.: AS-ThM9, **2**
Bersani, M.: AS-ThM9, **2**

— C —

Carlson, B.: AS-ThM7, **1**

— D —

Dahotre, N.B.: AS-ThM10, **2**
Donley, M.S.: AS-ThM6, **1**

— E —

Engelhard, M.H.: AS-ThM5, **1**

— F —

Fairbrother, D.H.: AS-ThM4, **1**

— G —

Gaskell, K.J.: AS-ThM3, **1**

— J —

Jach, T.: AS-ThM8, **1**

— K —

Kasten, L.S.: AS-ThM6, **1**

— L —

Landree, E.: AS-ThM8, **1**
Langley, L.A.: AS-ThM4, **1**
Lea, A.S.: AS-ThM5, **1**

— M —

Meyer, III, H.M.: AS-ThM10, **2**
Mrozek, P.: AS-ThM7, **1**

— N —

Nagarajan, V.: AS-ThM9, **2**

Nayak, S.: AS-ThM10, **2**

Nguyen, T.H.: AS-ThM4, **1**

— P —

Powell, C.J.: AS-ThM1, **1**

— Q —

Qiu, Z.Q.: AS-ThM11, **2**

— R —

Ramesh, R.: AS-ThM9, **2**
Rotenberg, E.: AS-ThM11, **2**

— S —

Sherwood, P.M.A.: AS-ThM3, **1**
Smith, M.M.: AS-ThM3, **1**
Smith, N.V.: AS-ThM11, **2**

— V —

Vanzetti, L.: AS-ThM9, **2**

— W —

Won, C.: AS-ThM11, **2**
Wu, Y.Z.: AS-ThM11, **2**

— Z —

Zhao, H.W.: AS-ThM11, **2**

Zhao, T.: AS-ThM9, **2**