

Applied Surface Science Division

Room 307 - Session AS-MoM

Materials Analysis (including Small Dimensions and Synchrotron)

Moderator: F.A. Stevie, Lucent Technologies

8:20am AS-MoM1 Synchrotron Based Low Z Materials Analysis, D.A. Fischer, National Institute of Standards and Technology **INVITED**

A new soft-x-ray (C,N,O,F) materials science end station to study the structure and chemical nature of diverse materials at the National Synchrotron Light Source has been designed, built and commissioned. Practical industrial problems, are currently being investigated, such as model catalyst systems, polymer surfaces and their interfaces, hard disk lubricant chemistry, self assembled monolayers and high Tc super conducting tapes. This presentation will describe the Dow / NIST soft x-ray materials characterization facility and review the on going NEXAFS research from a scientific and practical perspective. The experimental station, which delivers state-of-the-art intensity, resolution, and detection sensitivity is the result of a collaboration between NIST, The Dow Chemical Co., Brookhaven National Laboratory, and NIST Small Business Innovation Research (SBIR) awardees, International Radiation Detectors and Osmic Inc. Polarized ultra soft x-rays from the newly configured and upgraded NSLS U7A beamline are utilized as a search light for chemical bond identification, quantification, and orientation via the NEXAFS technique. Utilizing electron and fluorescence detection methods the surface (5nm) and bulk (200nm) structure and chemistry can be compared and contrasted simultaneously.

9:00am AS-MoM3 Contribution of a Fano Resonance and Pt-H EXAFS in the Pt L₂₃ XANES of Supported Pt Particles: Application to Materials Characterization, D.E. Ramaker, George Washington University; B.L. Mojet, Utrecht University, The Netherlands, Netherlands; J.T. Miller, Amoco; D.C. Koningsberger, Utrecht University, The Netherlands, Netherlands

The electronic and geometric effects induced by hydrogen chemisorption on small platinum particles supported on high surface area γ -Al₂O₃ and zeolite LTL, were studied by XANES. A new subtraction procedure was developed to separate the electronic from the geometric effects. The Pt-H anti-bonding state (electronic effect) was isolated and was found to have a Fano-resonance line shape. In addition, a significant Pt-H EXAFS scattering (geometric effect) was found for energy values between 0 and 20 eV. The resonance energy, width, and background phase parameter were obtained by least squares fit of the Fano lineshape function to the isolated experimental lineshape. For the Pt/LTL samples the shape and energy of the Fano resonance was found to strongly depend on the acidity/alkalinity of the support material, implying a direct influence of the support on the electronic properties of the Pt particles. The identification of the resonance and Pt-H EXAFS features on these Pt catalysts demonstrates the potential of this new analysis technique for the study of hydrogen chemisorption, metal-promoter, and metal-support effects in catalysis, electrochemistry, and nanoscale technology.

9:20am AS-MoM4 An Investigation of the Surface Chemistry of Lubricant Additives on Steel by NEXAFS Spectroscopy, T.S. Rufael, J.K. Mowlem, Texaco Inc.; D.A. Fischer, National Institute of Standards and Technology

Molecular level investigations of highly complex adsorption systems, such as the lubrication process in automotive parts, provide a challenge for mechanistic understanding and spectroscopic identification of surface intermediates. In this study, Near-Edge X-ray Absorption Fine Structure Spectroscopy is used to probe the surface reactions of a well-known anti-wear additive, zinc dialkyl dithiophosphate (ZDDP), and a novel friction modifier, molybdenum dithiocarbamate (MoDTC) on a polished steel alloy surface. Thin films from representative concentrations of ZDDP and MoDTC in base oil have been studied individually as well as in combination with each other following thermal processing at temperatures conducive for ZDDP decomposition. Soft X-ray absorption at the oxygen K-, carbon K-, iron-L, zinc L-, and molybdenum M-edges has been used to examine the structural and chemical changes taking place at the interface. In addition, we have investigated the effect of a model pro-oxidant, cumene hydroperoxide (CHP), on the above systems. We discuss the suitability of NEXAFS spectroscopy to study such complex adsorption systems by presenting results from these model lubricant systems.

9:40am AS-MoM5 Small Area Analysis: The Synergism of FIB/TEM Instrumentation, L.A. Giannuzzi, B.I. Prenitzer, J.L. Drown, University of Central Florida; S.R. Brown, Cirent Semiconductor; T.L. Shofner, Bartech Group; R.B. Irwin, F.A. Stevie, Cirent Semiconductor **INVITED**

The use of transmission electron microscopy (TEM) as a routine characterization tool has increased over the years, particularly in the microelectronics industry, as a result of the decreasing dimensions of the design rules used in integrated circuits. The need to detect compositional analysis from site specific regions is also a primary concern. TEM is often the only technique that may resolve microstructural and compositional features that are present in complex material components. Until recently, the production of a suitable TEM specimen has often been the limiting factor in TEM analysis. However, the use of focused ion beam (FIB) instrumentation for the production of site-specific TEM specimens has greatly increased the TEM productivity. The versatility of the novel FIB lift-out technique has also allowed for little or no prior sample preparation. In addition, since the bulk sample can be preserved, several TEM specimens may be acquired from the same sample between processing steps. This technique has been expanded to the TEM specimen preparation of microelectronic materials, metals, ceramics, composites, multi-layers, biological materials, fibers, and powders in both cross-section and plan view section.

10:20am AS-MoM7 Small Area X-ray Photoelectron Spectroscopy using a Spherical Mirror Analyzer, B.J. Tielsch, S.P. Page, Kratos Analytical Ltd, United Kingdom; D.J. Surman, Kratos Analytical, Inc.; S. Scierka, Millenium Inorganic Chemicals; E.A. Thomas, J.E. Fulghum, Kent State University

The analysis of heterogeneous or patterned samples by XPS frequently requires both imaging and small area spectroscopy. As the spatial resolution in photoelectron images decreases, the need for improvements in high energy resolution, small area spectroscopy increases. In most cases, the current limit on small area spectra is ~ 10 microns using either a virtual probe or a focussed x-ray spot. The Kratos AXIS Ultra uses a spherical mirror analyzer for real-time, parallel image acquisition, enabling images with a spatial resolution of 2-4 microns to be acquired in minutes. Spectra are routinely acquired using the hemispherical analyzer, however, the spherical mirror analyzer can be utilized by acquiring a series of images at different binding energies. Spectra can then be calculated from any point within the image by plotting the intensity of the selected pixels as a function of binding energy. We will show spectra determined from images for a variety of samples. The energy resolution obtained with the spherical mirror analyzer will be shown to be comparable to the hemispherical analyzer. The speed of image acquisition means the analysis time is similar to the time required for acquisition of small area spectra in some cases, although better spatial resolution is possible. Using this "images-to-spectra" mode, spectra can be obtained from areas of approximately 5 microns. The spatial resolution will be demonstrated using test samples containing features of known size, and the utility of the "images-to-spectra" mode will be evaluated using composites and polymer blends. This research has been partially supported by NSF (CHE-9631702, CHE-9613880, DMR89-20147) and 3M.

10:40am AS-MoM8 Analysis of Heterogeneous Polymer Samples using XPS, J.E. Fulghum, E.A. Thomas, A.C. Ferryman, Kent State University; B.J. Tielsch, Kratos Analytical, United Kingdom

The surface of samples prepared from polymer blends may have a composition different from that of the bulk material. If the polymers are not completely miscible, lateral heterogeneities on the surface may exist as well. Surfaces which are heterogeneous on the scale of microns can be characterized by XPS through small area spectroscopy and imaging. Determining the existence of concentration gradients within the XPS sampling depth is difficult for such samples, however. Several polymer blend systems will be used to demonstrate the near-surface and bulk gradient information which can be obtained from polymer blends if a combination of XPS experiments is utilized. Significant information can be obtained from quantitative analysis of the valence band, and this will be compared to results utilizing core level spectra. Polymer systems to be discussed include blends of modified polyimides used in liquid crystal displays, poly(vinyl chloride) and poly(methyl methacrylate) (PVC and PMMA) blends which have been previously studied using XPS, TOF-SIMS and FTIR, and polyacrylates. This work has been partially supported by NSF (CHE-9631702, CHE-9613880, DMR89-20147) and 3M.

Monday Morning, November 2, 1998

11:00am **AS-MoM9 TOF-SIMS analysis of Atmospheric Aerosol, R.E. Peterson, B.J. Tyler**, Montana State University

We are evaluating the potential for using TOF-SIMS to study single particles from atmospheric aerosol. X-ray analysis has commonly been used to analyze the composition of single particles but there are several limitations to X-ray analysis. Principally, x-ray analysis cannot be used to study organic compounds in the aerosol, it offers low sensitivity for light elements common in crustal material and it cannot distinguish isotopes. TOF-SIMS has the potential to provide superior performance in these areas. Samples of naturally occurring and anthropogenic atmospheric aerosol were collected on Millipore fluoropore (PTFE) filters in southwest montana. Sections of the filters were imaged using a PHI TRIFT I instrument with a Ga primary ion source. Both positive and negative ion images were studied. A large number of particles could be distinguished on the filter surfaces, which were absent on control samples. Particle diameters varied from 2 to 10 μm . Hydrocarbons, silicon, aluminum, potassium, calcium, and sulfates were associated with the particles found in the images. These correspond to common sources of aerosol in the region including crustal dust, partially neutralized sulfuric acid droplets, and carbonaceous compounds associated with forest fires. The aerosol found indicate a combination of particles originating from gas to particle conversion and surface sources

11:20am **AS-MoM10 Evaluation of Ge Based Detectors for Small Area Analysis, X. Lu, J.R. Kingsley**, Charles Evans & Associates

The development and commercial availability of Energy Dispersive X-ray Spectroscopy (EDS) detectors employing Ge rather than Si detectors, combined with thermally assisted Field Emission Scanning Electron Microscopy (FE-SEM) has allowed EDS to be re-evaluated as a small area analytical tool. The higher spectral resolution of the Ge EDS detector allows lower accelerating voltage to be effectively used for elemental identification, while the thermally assisted FE-SEM has the ability to maintain a usable amount of current, at low voltage, in a spot smaller than the inherent interaction volume. In this paper we will characterize the performance of just such a system when used for particle and IC cross section analysis.

11:40am **AS-MoM11 Detection and Passivation of Surface States in InP by Thermally Stimulated Exo-electron Emission Spectroscopy, S.S. Hullavarad¹, S.V. Bhoraskar**, University of Pune, India

InP based devices are rapidly becoming dominant in high mobility and optoelectronic device technologies. InP has an electron mobility that is three times that of conventional Si. In principle, devices built with InP should be faster by this factor than the comparable Si devices. However, the surface properties of InP have prevented its use in MIS devices. Devices based on InP suffer from defects that occur in the material which act as charge traps, changing the bias of the device and so impeding its performance. We have attempted to tailor the surface of InP so as to reduce the surface state density by tying up the dangling bonds with proper passivant. The energy distribution and relative densities of such electronically active surface states in InP have been studied using thermally stimulated exo-electron emission spectroscopy (TSEE). This novel and relatively simple technique has high sensitivity for detecting the surface states which is difficult to be assessed by other techniques. Here this technique is successfully used for the first time for detecting the pinned Fermi positions of the Fermi level in n-(100) InP. The TSEE measurements were performed in the high vacuum conditions using channel electron multiplier, in the clean environment. The surface states in InP in the presence of its native oxide were detected when the sample was heated from 175 K to 450 K. TSEE peaks were identified at 207.5 K and 350 K. The energies of these defects were calculated to be 0.43 eV and 0.74 eV respectively. The surface state passivation of pinned Fermi level is achieved by ECR coupled thiophene plasma polymerization. The constituents of the polymerized InP surface were identified using energy dispersive X-ray analysis (EDXAS). Microwave assisted electron cyclotron resonance (ECR) plasma was used to deposit thin films of passivating overlayers. Polythiophene (CH₃CH₂S) was deposited by injecting the monomer thiophene into the reaction chamber pre-evacuated to a base pressure of $\sim 10^{-5}$ Torr. The TSEE spectrum recorded after the deposition of polymer differed from the one which was recorded earlier. The peak in the TSEE appearing at 207.5 K has disappeared. The very fact that this corresponded to the pinned Fermi level in InP shows that the plasma polymer has been effective in chemically passivating the surface.

¹ Best ASSD Student Paper Competitors

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