Applied Surface Science Division
Room 307 - Session AS-ThM

Gaede-Langmuir Award Address and Quantitative Surface Analysis

Moderator: P.M.A. Sherwood, Kansas State University

9:00am **AS-ThM3 Resolution Enhancement of XPS Spectra by Maximum Entropy Deconvolution***, S.J. Splinter,* B.C. Research Inc., Canada*; **N.S. McIntyre,*** The University of Western Ontario, Canada **INVITED**

Detailed Analysis of XPS spectra is often limited by the resolution available in the measurements. Energy resolution improvement can be achieved in practice by monochromatization of the exciting x-rays and/or by very high energy resolution analysis of the emitted photoelectrons through improved instrumentation. Both of these approaches, however, require expensive high-intensity photon sources. This added cost therefore provides an acute motivation for the development of a reliable computational means for resolution enhancement. In this talk, I will describe a method for enhancing the energy resolution of photoelectron spectra by deconvolution based on the maximum entropy method (MEM). I will first review the theory of deconvolution as applied to XPS and briefly discuss previous work in this area. I will then present the mathematical description of MEM, explaining why this represents a better approach to take, and describe the algorithmic and computational details used to solve the large-scale non-linear constrained optimization problem. Several representative examples of simulated and experimental spectra will be presented.

9:40am **AS-ThM5 Evaluation of Calculated and Measured Electron Inelastic Mean Free Paths***, A. Jablonski,* Polish Academy of Sciences, Poland*; **C.J. Powell,*** National Institute of Standards and Technology

NIST will release a database in 1998 that provides values of electron inelastic mean free paths (IMFPs) for use in surface analysis by AES and XPS. The database includes IMFPs calculated from optical data and measured by elastic-peak electron spectroscopy. IMFPs can also be obtained from the predictive formulae proposed by Seah and Dench, Tanuma et al., and Gries. We present here an evaluation of calculated and measured IMFPs for seven elemental solids (Al, Si, Ni, Cu, Ge, Ag, and Au); these solids were selected because, for each, there were two or more independent IMFP calculations and two or more independent IMFP measurements. For each element, calculated IMFPs have been compared, measured IMFPs have been compared, and calculated and measured IMFPs have been compared. Our preliminary results indicate that the best agreement among the calculated IMFPs (as determined from mean relative deviations with respect to a common fitted curve) is found for Al, Ni, and Ag. Similarly, the best agreement among the experimental values is found for Si, Cu, and Ge, and the best agreement between calculated and measured values is found for Cu, Ag, and Au. We will discuss reasons for the differences found in our comparisons.

10:00am **AS-ThM6 Development of Well Defined Reference Samples for ARXPS Depth Profiling Studies***, **B.J. Tyler,** S.J. Hunt,* Montana State University

Quantifying the changes in material composition in the near surface region is important for a wide range of research problems. With inorganic and metallic samples, this information can often be obtained by sputter depth profiling. However, for organic samples, ion sputtering typically destroys the chemical structures of interest before they can be measured. As a result, angle resolve XPS is the preferred method for studying concentration depth profiles (CDP) for polymeric materials and organic thin films. As the interest in organic surfaces has grown, demand for quantitative measures of CPDs for these surfaces has also grown. While qualitative interpretation of ARXPS results is routine, there are many barriers to quantitative calculation of concentration depth profiles (CDPs) from ARXPS results. Many algorithms have been developed for this purpose but determining accurate confidence limits for CDPs, which are calculated with these algorithms, is currently the most significant challenge for quantitative depth profiling with ADESCA. One barrier to assessing the accuracy of CDPs is lack of adequate reference samples. We have evaluated the use of self-assembling monolayers, spin cast polymers, and plasma deposited films for their potential as standards for ARXPS work. The thin films were made on ultra smooth gold and silca substrate. Surface roughness and film thickness have been measured with AFM. ARXPS data for the samples was measured on both a PHI 5600 XPS system and a SSI s-probe. Resulting depth profiles calculated with several algorithms will be presented.

10:20am **AS-ThM7 Trajectory Projection Factor Analysis***, **D.J. Pocker,** B.R. York,* IBM SSD

Linear least squares (LLS) analyses of arrays of Auger or ESCA spectra (as from depth profiles, line scans or maps) run into problems when the data does not contain regions with pure spectra for one or more of the compounds. In addition, target factor analysis (TFA) encounters problems when there is not prior knowledege of the profiles for each compound. We present here an eigenanalysis and coordinate transformation method which straightforwardly extracts spectra for the pure compounds along with their associated profiles from arrays with overlapping spectra of up to 4 compounds. In the method, the profiles for the mathematically distinct eigenspectra are plotted against each other, yielding a TRAJECTORY through the orthogonal eigenspace. PROJECTION of this trajectory onto/into a well chosen plane or volume then allows a simple transformation of coordinates to define a non-orthogonal, chemically interesting space. From this, the pure compound spectra and profiles are easily computed. (The limit of 4 is from the graphical nature of the analysis. The concept extends to an arbitrary number of compounds. Also, for favorable 4 compound cases, overlaps as bad as "never fewer than 3" can be treated.)

10:40am **AS-ThM8 Quantitative High-Resolution Imaging with Sputter-Initiated Resonance Ionization Spectroscopy***, **K.F. Willey,*** Atom Sciences, Inc.*; H.F. Arlinghaus,* Westfälische Wilhelms-Universität Münster, Germany*; T.J. Whitaker,* Atom Sciences, Inc.

The demand for sub-micron lateral analysis, as a result of decreasing material size, has been met by the development of liquid metal ion gun (LMIG) sources capable of achieving spot sizes less than 50 nm. The trade-off however, is the reduction in ion beam current at the sample. Therefore, highly sensitive detection techniques are required. Our technique, Sputter-Initiated Resonance Ionization Spectroscopy (SIRIS), incorporates resonant ionization of sputtered neutral particles with time-of-flight mass detection. The two major advantages this approach has over conventional SIMS are that analysis of neutrals generally increases the detection efficiency by at least two orders of magnitude, and that resonance ionization nearly eliminates mass interferences. Additionally, analysis of neutrals substantially removes matrix effects, which is crucial for quantitative surface analysis. Sputtering is achieved with a gallium LMIG, a mass-filtered microbeam ion gun, and a mass-filtered low-energy sputtering ion gun. Sub-micron lateral resolution and few nanometer depth resolution have been obtained by eroding the sample with the low-energy ion gun while analyzing with the LMIG. In our presentation, we will describe the SIRIS technique and its dynamic range for quantitative analysis and imaging capabilities as they pertain to semiconductor research. In particular, Ge and B depth profiles on near one µm spot size and Cu trace element images obtained from Cd precipitates in CdZnTe films will be presented.

11:00am **AS-ThM9 Quantitative Detection of Metals in Organic Matrices by Laser-SNMS***, **A. Schnieders,** H.F. Arlinghaus, A. Benninghoven,* Universität Münster, Germany

TOF-SIMS and Laser-SNMS have been established as powerful tools for high sensitive trace analysis of elements in inorganic materials, like alloys and semiconductors. Detection limits for almost all elements are in the range of 10@super 8@ - 10@super 9@ particles/cm@super 2@ of a single monolayer. For many analytical applications comparable sensitivities for the detection of metals in organic matrices are required, e. g. in life sciences. Unfortunately, TOF-SIMS is limited by the low secondary ion yields for metals in these matrices. The sensitivity is several decades lower than for the same metals on semiconductor surfaces. Because of the decoupling of the desorption and ionization processes, the use of Laser-SNMS is a promising approach to get rid of this limitation. Laser-SNMS combines the advantages of ion beam induced desorption with the possibility to optimize the ionization efficiency. For our investigations we applied nonresonant multiphoton ionization allowing a nonselective and highly efficient postionization of sputtered neutrals. As a model system for metals in organic matrices we prepared submonolayer coverages of several metals (Be, Cr, Mn, Fe, Co, Ni, Mo, W) on different polymer foils (polycarbonate, polyimide, and polyvinylidenechloride) by sputter deposition. We used these standards for quantification. Relative sensitivity factors of the respective elements are found to be similar to those for material sputtered from alloys or semiconductors within a factor of 3. The detection limits are in the range of 10@super 8@ to 10@super 9@ particles/cm@super 2@. We also used Laser-SNMS for the identification of the active center of a purple acid phosphatase. Our results demonstrate the detection and identification of single metal atoms in organic

macromolecules with an atom concentration down to < 100 ppm. The use of resonant photoionization lowers the detection limits for similar systems by further decades.

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