

QSA-10 Topical Conference Room 320 - Session QS-MoM

Advances in Quantitative Surface Analysis

Moderator: C.J. Powell, National Institute of Standards and Technology

8:20am QS-MoM1 Modules for an XPS Expert System: Applications in Corrosion Science, *J.E. Castle*, University of Surrey, UK **INVITED**

Expert Systems (ES) can guide users in application of XPS. @footnote 1-6@ Guidance requires modules of the ES to be tailored to a particular group, e.g., corrosion scientists. This group, which has defined needs and a history of using XPS, could benefit from automated knowledge retrieval. In creating a set of rules, the requirements are defined and matched to the information that might be delivered by XPS, e.g.: the mean surface composition and relation to the bulk; the location of any marker elements; the thickness of overlayers, e.g., a contamination layer and an oxide or similar layer; evidence for graded composition such as enrichment of an alloying element in the oxide or metallic undersurface; valance states and a trial stoichiometric composition. Reminders of further opportunities should also be provided, possibly by use of on-screen wizards. @footnote 4,5@ In proposing this ES module emphasis will be placed on the cost-effective provision of basic information from the 'survey scan'. The rules have provenance from prior discussion and publication by international workshops such as those sponsored by IUVSTA. @footnote 1,3,6@ The rule base will be most useful when it is embedded in the controlling system for the spectrometer, so that some degree of knowledge based acquisition is possible, but would be equally suitable for stand alone, retrospective analysis. Both outcomes make a demand on costly resources that in the end will have to be provided by the user community. It is hoped that this feasibility study will show that, for corrosion scientists, this is worthwhile. @FootnoteText@ @footnote 1@M-G Barthes-Labrousse, Surf.Interface Anal. 26 p72 - 91 (1998) @footnote 2@J.E.Castle and M.A.Baker, J. Elec Spec Rel. Phenom., 105 p245 - 256 (1999) @footnote 3@L.Kover, Surf. Interface Anal. 29 p671 - 716 (2000) @footnote 4@J. E. Castle, PV 2001 - 5, C.R.Clayton et al. Eds. The Electrochemical Soc., NJ. pp1-14(2001) @footnote 5@J.E.Castle, Surf.Interface Anal. 33 pp 196 - 202 (2002) @footnote 6@ Report of St Malo Workshop, to be pub.

9:20am QS-MoM4 Auger Electron Spectroscopy: Reducing Measurement Uncertainty, *J.D. Geller*, Geller MicroAnalytical Laboratory **INVITED**

Quantitative analysis using Auger electron spectroscopy (AES) is most commonly performed using pure element sensitivity factors. The accuracy of the technique can be quite good for materials such as stainless steels where many of the elements have adjacent atomic numbers and similar densities. However, in most other materials errors well over 100% of the accepted true value are commonplace. The reasons for this will be discussed and different methods for quantifying data will be compared for their effectiveness. Accuracy, defined as the difference between the accepted true value and the result of an analysis, with Auger electron spectroscopy has seen very slow improvements over the years. There have been relatively very few technical papers addressing this important subject. By contrast, highly accurate quantitative analysis with the electron probe micro analyzer (EPMA) developed very quickly to the point where accuracies in the range of a few percent on a relative basis are commonly reached. Programs for converting x-ray intensities to concentrations following the ZAF (where Z is atomic number correction, A the absorbance correction, and F the fluorescence correction) procedures are available both in the public domain as well as from all the manufacturers of x-ray spectroscopic equipment. For AES there are no commercially available programs beyond the sensitivity factor approach. This work evaluates the current matrix effect corrections approaches (Sekine, et al) to that using elemental sensitivity factors from measurements with compounds. Sensitivity factors for several experimentally collected stoichiometric carbides, silicides, phosphides and sulfides are compared with those calculated from pure element sensitivity factors using matrix effect corrections. The factor with the greatest uncertainty was found to be preferential ion sputtering which is not included in any of the corrections. Sekine, et al, Evaluation of Correction Accuracy of Several Schemes for AES Matrix Effect Corrections, Surface and Interface Analysis, Vol. 15, 466-472 (1990).

10:20am QS-MoM7 Molecular Characterization of Biomaterials with ToF-SIMS Imaging, *N. Winograd*, Penn State University **INVITED**

It is now feasible to employ ion beams to desorb molecules directly from a variety of complex matrices. Here we show that it is possible to examine frozen-hydrated biological interfaces prepared using a special freeze-fracture protocol. The results demonstrate that it is possible to unravel dynamical events such as chemical fluctuations associated with domain structure in cellular membranes. This strategy allows the distribution of molecules within these matrices to be determined with high lateral resolution. Fracturing criteria for preserving chemical distributions have proven to be much more stringent than morphological cryo-electron microscopy studies. Two examples will be discussed. In the first instance, we report on the characterization of liposome particles that are about 50 microns in diameter. We have captured each stage of a fusion event between two liposomes and have shown that membrane structure during fusion ranges from specific domains that then migrate across the interface to produce a homogeneous, fluid-mosaic membrane. In the second instance, several different possible fracture planes from single biological cells have been imaged to understand further the process of freeze fracture and TOF-SIMS imaging of cellular membranes. Sensitivity is still problematic for this type of mass spectrometry. We present recent imaging data using a C60+ ion source that increases the yield of biomolecules by more than a factor of 1000. Combined with the freeze-fracture protocols, this technology holds the promise to define the biology of cellular membrane surfaces at the molecular level.

11:20am QS-MoM10 Extrinsic and Intrinsic Excitations in Ge and Si Photoelectron Spectra, *L. Kövér*, *Z. Berényi*, Institute of Nuclear Research of the Hungarian Academy of Sciences, Hungary; *S. Tougaard*, University of Southern Denmark, Denmark; *F. Yubero*, Instituto de Ciencia de Materiales de Sevilla, Spain; *I. Cserny*, *J. Végh*, *J. Tóth*, *D. Varga*, Institute of Nuclear Research of the Hungarian Academy of Sciences, Hungary; *W. Drube*, *T. Eickhoff*, HASYLAB at Deutsches Elektronen-Synchrotron DESY, Germany

Studying excitations accompanying deep core photoemission and Auger transitions in solids of great practical interest is important for understanding solid state effects@footnote 1@ on such transitions and for revealing the electronic structure of these systems. Here we report our results for (Ge 1s,2s; Si 1s) core photoelectron spectra excited by X-rays of different energies. Photoelectron spectra were obtained using the Tunable High Energy XPS facility at the BW2 beamline of HASYLAB. @footnote 2@ while the electron energy loss spectra reflecting the effects due to inelastic scattering (extrinsic losses) were measured with the home built ESA-31 electron spectrometer. @footnote 3@ The background corrected spectra are compared to model spectra calculated within the frame of a theory@footnote 4@ developed to describe both extrinsic and intrinsic (due to the appearance of the core hole) losses in XPS experiments. In addition, the ratio of the probabilities of extrinsic and intrinsic plasmon creation has been derived analyzing the excited plasmon spectra and is compared to the ratio obtained from the theory and from an other experimental approach. In a reasonable agreement with the theory, our analysis of the measured spectra shows a significant contribution from intrinsic excitations. Supported by OTKA T038016 and IHP-Contract HPRI-CT-1999-00040/2001-00140 (EC). @FootnoteText@ @footnote 1@ L. Kövér, Zs. Kovács, J. Tóth, I. Cserny, D. Varga, P. Weightman and S. Thurgate, Surf. Sci., 433-435(1999)833. @footnote 2@ W. Drube, T. M. Grehk, R. Treusch and G. Materlik, J. Electron Spectrosc. Relat. Phenom., 88-91(1998)683. @footnote 3@ L. Kövér, D. Varga, I. Cserny, J. Tóth and K. Tökési, Surf. Interface Anal., 19(1992)9. @fooonote 4@ A. Cohen-Simonsen, F. Yubero and S. Tougaard, Phys. Rev. B56(1997)1612.

11:40am QS-MoM11 Multivariate Analysis for XPS Spectral Imaging@footnote 1@, *D.E. Peebles*, *J.A. Ohlhausen*, *P.G. Kotula*, Sandia National Laboratories

The acquisition of complete spectral images for x-ray photoelectron spectroscopy (XPS) is a relatively new approach, although it has been used with other analytical spectroscopy tools for some time. This technique generates full spectral information at every pixel of an image, in order to provide a complete chemical mapping of the imaged surface area. Multivariate statistical analysis techniques applied to the spectral image data provide a way to sort through this large block of data to determine the chemical component species present as well as their distribution and concentrations, with minimal data acquisition and processing times. The benefits of multivariate analysis of the spectral image data include significantly improved signal to noise and improved spatial resolution, which are achieved due to the large number of data points included in the

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image. In this paper, we will illustrate the signal to noise and spatial resolution obtained from a Magnification Reference Standard at a series of spectral image acquisition times, with a direct comparison of the raw images to the multivariate processed data. We will demonstrate the elemental separation and chemical discrimination possible with Sandia's novel multivariate statistical analysis approach for both limited spectral region acquisition as well as more complete spectral imaging data sets. It will be shown that Sandia's techniques provide efficient methods for deriving physically realistic chemical components without user input other than the spectral data matrix itself. @FootnoteText@ @footnote 1@ This work was completed at Sandia National Laboratories, a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

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