Applied Surface Science
Room 206 - Session AS-WeM

Essential Tools for Surface Analysis

Moderator: J.E. Fulghum, University of New Mexico

8:20am **AS-WeM1 TOF-SIMS: Accurate Mass Scale Calibration***, F.M. Green,* ***I.S. Gilmore,*** National Physical Laboratory, UK*; M.P. Seah,* National Physical Laboratory, UK, United Kingdom

A study is presented of the factors affecting the calibration of the mass scale for TOF-SIMS. At the present time, analysts achieve a mass accuracy of only 150 ppm for large molecules (647 amu) and for smaller fragments of < 200 amu may typically be 60 ppm. The instrumental stability is 1 ppm and better than 10 ppm is necessary for unique identification of species. In the recent interlaboratory study@footnote 1@ only 3 instruments out of 32 were within 10 ppm for smaller fragments. The experimental uncertainty can lead to unnecessary confusion where peaks are wrongly identified or are ambiguous. Here we study in detail the instrumental parameters of a popular reflection TOF-SIMS. The effect of the ion kinetic energy, emission angle and other physical and instrumental operating parameters on the measured peak position are determined. This clearly shows why molecular and atomic ions have different mass accuracy and peak shapes. These data provide the basis for a coherent procedure for optimising the instrumental settings for accurate mass calibration and rules by which inorganics and organics may be incorporated. This leads to generic sets of ions for mass calibration, which, used for re-calibration, improves the mass accuracy of the interlaboratory study data@footnote 1@ by up to a factor of 4. Now, 12 instruments out of 32 are within the 10 ppm range. The effects of extrapolation beyond the calibration range are discussed and a recommended procedure given to ensure that accurate mass of large molecules is achieved within a selected uncertainty. One bonus of this study is that the instrument can now be operated in a regime with good energy discrimination to study the fragmented energies of molecules. We shall discuss how this compares with data from G-SIMS@footnote 2@ and supports the G-SIMS concept. @FootnoteText@ @footnote 1@ I S Gilmore, M P Seah and F M Green, submitted Surf. Interface Anal.@footnote 2@ I S Gilmore and M P Seah, Appl. Surf. Sci., 161 (2000), p. 465.

8:40am **AS-WeM2 Quantitative XPS: Quadrupole Terms, Shake-Up, Shirley Background and Relative Sensitivity Factors***,* ***M.P. Seah,*** National Physical Laboratory, UK, United Kingdom*; I.S. Gilmore,* National Physical Laboratory, UK

An analysis is provided of the XPS intensities measured in the NPL XPS database for 46 solid elements. This present analysis does not change the previous conclusions concerning the excellent correlation between experimental intensities following deconvolution using the angle-averaged REELS data and the theoretical intensities involving the dipole approximation and Scofield's cross sections. Here, we test the more recent calculations for cross sections by Trzhaskovskaya et al with quadrupole terms and find that their cross sections diverge from the database by up to a factor of 2. The quadrupole angular terms lead to small corrections also evaluated in the present analysis. Measurements of the extent of shake-up for the 46 elements broadly agree with theoretical calculations but details of the observed element-to-element variation are not reproduced in those calculations. The predicted theoretical constancy in the shake-up contribution implies that the use of the Shirley background will lead to a peak area that is a constant fraction of the true peak area including the shake-up intensities. If this were the case, the peak areas using the Shirley background would be a valid measure of intensity. We would therefore expect that the ratio of the peak area using the Shirley background to the intensity calculated using the cross sections, etc, would be a constant value, less than unity, with a reasonably small scatter. Unfortunately, the variability of the shake-up contribution, and the variability with which the Shirley background reproduces the angle-averaged background under the peak, itself, both combine to leave a 38% relative standard deviation in this ratio. The Shirley background thus appears to be a poor method for general quantitative analysis. Its use may need to be limited to specific situations where the sensitivity factors have been obtained from reference samples similar to those being analysed.

9:00am **AS-WeM3 SURFACE SCIENCE SPECTRA: The AVS Surface Science Database for the Surface Spectroscopy Community***,* ***S.W. Gaarenstroom,*** General Motors R&D Center **INVITED**

The surface spectroscopy community shares high-quality spectral data on hundreds of materials by means of the AVS Surface Science Database. Most of the shared spectral data is obtained by x-ray photoelectron spectroscopy, but Auger electron spectroscopy, secondary ion mass spectrometry, electron energy loss spectroscopy and other techniques are also represented. This database effort, named SURFACE SCIENCE SPECTRA, was launched in 1992. The SSS developers benchmarked and built upon the database efforts made for other kinds of spectroscopies (such as infrared spectroscopy, mass spectrometry, and x-ray diffraction), but were also attentive to the special needs in the surface science community. The contributors to the spectral database are from the worldwide surface science community at large (more than 450 individual contributors from more than 110 different institutions). The evaluators of the database are also from the entire surface science community, because all data records are peer-reviewed prior to acceptance and entry into the database. Simultaneous with the launch of the journal product of the SURFACE SCIENCE SPECTRA database, massive changes began in the publishing world's electronic technology and the individual scientist's preferences for accessing information. While the descriptors in each individual data record have changed only minimally in the years since the database launch, the delivery mechanism changed continually and will continue to change. The current conversion of the on-line journal to XML publishing technology provides new opportunities to inexpensively add useful features for the benefit of the database users.

9:40am **AS-WeM5 Software Package to Determine @epsilon@(k,@omega@) from Analysis of REELS***,* ***S. Tougaard,*** University of Southern Denmark, Denmark*; F. Yubero,* Inst. de Ciencia de Materiales de Sevilla, Spain

Engineering of new thin solid films of varying composition are of current high technological interest. Methods to determine the electronic properties of thin films are therefore of increasing importance. The complex dielectric function @epsilon@(k,@omega@) contains valuable information on the electronic structure. The effective single scattering cross section can be determined from analysis of reflected electron energy loss spectra (REELS)@footnote 1@ and a semi-classical dielectric response model for REELS was also developed.@footnote 2,3@ It has been shown how this can be applied to determine @epsilon@(k,@omega@) from analysis of experimental REELS. This provides an intesting technique because REELS is rather simple to apply, it is inexpensive, it is available in many laboratories and above all it can easily be applied to thin films of only a few nano-meters thickness grown on a supporting substrate. The complexity of the formulas has however been a hindrance for widespread use of the technique. To make it generally available, we decided to develop a software package with a user friendly graphical interface and interactive facilities. We hope that this tool will inspire more widespread use of this method to explore the electronic properties of solids and thin films. @epsilon@(k,@omega@) can also be used to make quantitative interpretation of the fundamental mechanisms in photo- and Auger electron spectroscopy and to calculate the inelastic mean free path for electrons in solids and determine the excitations that take place when the electron moves in the surface region or in the vacuum above the surface. The software, which is free of charge for non-commercial use, handles the theory developed in the following papers:. @FootnoteText@ @footnote 1@ S. Tougaard and I. Chorkendorff, Phys. Rev. B23 6570 (1987)@footnote 2@ F. Yubero and S. Tougaard, Phys. Rev B46, p. 2486 (1992)@footnote 3@ F. Yubero, J.M. Sanz, B. Ramskov and S. Tougaard, Phys Rev. B53, 9719 (1996).

10:00am **AS-WeM6 Complete Analysis of ToF-SIMS Spectral Images in a Research and Development Analytical Laboratory***,* ***V. Smentkowski,*** General Electric Global Research Center*; M. Keenan, J.A. Ohlhausen, P.G. Kotula,* Sandia National Laboratories

Time of flight secondary ion mass spectrometry (ToF-SIMS) spectral image raw data files contain a wealth of information since an entire mass spectrum is saved at each pixel in an ion image. Currently, few tools are available to assist the analyst in visualizing the entire raw data set and as a result, most of the measured data are never analyzed. Typically, the ToF-SIMS analyst manually selects a few species to monitor based upon input from the customer, knowledge of results obtained from similar past analysis, high peak intensity and/or unusual species detected in the spectrum. Manual analysis is complicated by the fact that little is known about real-life samples prior to analysis. The analyst is expected to perform rapid, cost effective, analysis and provide a complete description of the sample. Automated, non-biased, multivariate statistical analysis (MVSA) techniques are useful for converting the massive amount of data into a smaller number of components that are needed to fully describe the ToF-SIMS measurement. We are using AXSIA to perform MVSA on ToF-SIMS

raw data files. The advantages of AXSIA include: the ability to select the mass range of interest, the ability to bin the mass spectra from 0.001amu to 1amu, optimal scaling of the data to account for Poisson counting statistics, and the generation of intuitive results. Examples will be selected to demonstrate these advantages. We will also demonstrate that positive ion and negative ion raw data files collected on the same region of a sample can be concatenated. MVSA analysis of the concatenated data provides a complete description of the sample. The analytical insight provided by concatenated MVSA analysis would be difficult, if not impossible, to obtain via other routes. Sandia National Laboratories is 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.

10:20am **AS-WeM7 Principal Components Analysis of TOF-SIMS Data: Why, What, and How*, D.J. Graham,*** University of Washington **INVITED**

Even the simplest TOF-SIMS spectrum can be complex. A typical spectrum may contain hundreds of peaks, the intensities of which can be correlated. This complexity has led to the exploration and application of multivariate analysis (MVA) methods to TOF-SIMS data in an attempt to simplify analysis and maximize the information content extracted from the data. MVA of TOF-SIMS spectra has shown promise and success for spectra and images across many systems including self-assembled monolayers, proteins, and polymers. Due to this success, multivariate analysis of TOF-SIMS data is quickly becoming more standard within the surface analysis community, yet there have been no standards set regarding how to properly apply multivariate methods to TOF-SIMS data. It is important to make sure that as progress continues in the application of MVA methods to TOF-SIMS data, standards be established in the application of theses methods, and that effort be made in the optimization of these methods, and the education of the community. This talk will highlight important considerations in the use of PCA with TOF-SIMS data. Experimental design, peak selection, data preprocessing and data interpretation will be discussed as it pertains to PCA of TOF-SIMS spectra.

11:00am **AS-WeM9 Automated Peak Identification in a TOF-SIMS Spectrum*, H. Chen,*** *E.R. Tracy, W.E. Cooke, M.W. Trosset,* College of William and Mary*; D. Malyarenko,* INCOGEN Inc.*; D.M. Manos,* College of William and Mary*; M. Sasinowski,* INCOGEN Inc.

Although the high mass resolution, imaging capability and the high-throughput capability of mass fingerprint measurements have made TOF-SIMS one of the standard tools for research in surface analysis. A bottleneck is that TOF-SIMS produces very large raw data sets that must be preprocessed to identify the mass peaks for further analysis, especially when complex biological samples produce a large number of peaks. The accuracy of the mass assignment, which is critical when comparing mass fingerprints with databases, can be another limitation. Under survey conditions, the positions of the desired mass peaks are commonly not known beforehand, and TOF-SIMS peak-picking requires a procedure to distinguish mass peaks from background noise. Often, those peaks and their positions are identified manually. This introduces a subjective error due to the asymmetric peak line shape and to Poisson (counting) noise which has larger variance at larger peaks. This results in a degradation of the apparent machine performance and an inconsistency in the peak identification. We have developed an automated peak picking algorithm based on a maximum likelihood approach that effectively and efficiently detects peaks in a TOF-SIMS spectrum. The algorithm takes into account the underlying characteristic Poisson process and asymmetric peak line shape and produces maximum likelihood estimates of peak positions and amplitudes. It also simultaneously develops estimates of the uncertainties in each of these quantities. With this approach, we avoid the ambiguities involved in manual peak picking and mass assignments. We use the estimated peak positions, amplitudes and their uncertainties to align different spectra more accurately than is possible by using a few known calibrants. This precise peak summary is crucial for further multivariate analysis.

11:20am **AS-WeM10 More Information from Shorter Acquisition Times in XPS Imaging and Other Multivariate Surface Analytical Datasets*, P.J. Cumpson,*** National Physical Laboratory, UK

Quantification of multivariate datasets, such as XPS images, is a major area of research due to the impressive capability of modern instruments. It can, however, present challenges in terms of signal-to-noise and long acquisition times. A very simple but computationally-intensive Bayesian chemometric method@footnote 2@ for addressing this problem was published around ten years ago. With increasing personal computer speeds this has become not just more practical, but even very rapid today. This approach to electron counting statistics results in a novel quantification method that halves acquisition time, or equivalently, results in an increase in signal-to-noise of roughly a factor of 1.4, rising to 1.7 for the shortest acquisition time, noisiest images. This is not a ``black box'' statistical method, but a relatively simple way of building-in the assumption that the primary beam is fairly stable from pixel-to-pixel, which is certainly the case for modern XPS instruments. The method is potentially valuable in depth-profiling too. We show that combining this method with rapid Monte Carlo methods@footnote 3,4@ (whose routine use has also become much more practical recently) leads to several important new chemometric methods for count-limited, multivariate surface analytical data in general. @FootnoteText@ @footnote 1@ K Artyushkova and J E Fulghum in "Surface Analysis by Auger and X-ray Photoelectron Spectroscopy", Ed. D Briggs and J T Grant (IM Publications, Chichester UK, 2004).@footnote 2@ P J Cumpson and M P Seah, Surface and Interface Analysis, 18 (1992) 361.@footnote 3@ P J Cumpson, Surface and Interface Analysis 20 (1993) 727.@footnote 4@ D Ze-jun and R Shimizu in "Surface Analysis by Auger and X-ray Photoelectron Spectroscopy", Ed. D Briggs and J T Grant (IM Publications, Chichester UK, 2004). .

11:40am **AS-WeM11 Improvements in the Spatial and Spectral Resolution of X-ray Photoelectron Images through Multivariate Analysis and Multisensor Fusion*, K. Artyushkova,*** *J.E. Fulghum, L.R. Williams,* The University of New Mexico*; S.J. Hutton, S.J. Coultas,* Kratos Analytical Ltd., UK

Improvements in spectral and spatial resolution of imaging X-ray photoelectron data are of growing importance, as the chemical complexity of materials under study increases, and the size of features to be resolved decreases. In this work we use a combination of multivariate analysis methods (MVA) and multisensor image fusion to resolve photoelectron image features in components that are similar in chemistry and small in size, relative to the spatial resolution of the technique. Methods combining XPS image acquisition schemes with multivariate analysis were tested to facilitate analysis of multicomponent samples containing spectrally overlapped chemical components. Additional spatial distribution information can potentially by obtained through multisensor image fusion of atomic force microscopy (AFM) and XPS images. X-ray photoelectron spectroscopy (XPS) has a high energy resolution but relatively low spatial resolution. In contrast, AFM images have significantly higher spatial resolution. We report initial efforts to combine low resolution color images (XPS) and a high resolution monochromatic images (AFM) to produce a higher spatial resolution XPS images. The validity of these approaches will be demonstrated using patterned SAM samples with known chemistry and spatial morphology. Application of these methods will be shown using images from phase-separated polymer blends. This work has been partially supported by NSF CHE-0350666 and UNM.

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