Wednesday Morning, October 4, 2000

Material Characterization Room 207 - Session MC-WeM

Methods of Data Analysis

Moderator: D.G. Castner, University of Washington

8:20am MC-WeM1 Interpretation of the Shirley Background in XPS INVITED Analysis, J.E. Castle, University of Surrey, U.K.

The feature that is perhaps the most characteristic of an XPS spectrum, i.e. the step in background which accompanies every peak, is also its most enigmatic. The simple interpretation given in early texts was that the step is created by extrinsic losses as the electron travels through the material has not survived the work of Tougaard@footnote 1@ who has shown that the extrinsic losses build up rather slowly on the low kinetic energy side of the peak. In fact when the Tougaard function is subtracted from a typical peak there remains a peak with a considerable tail. Interpretation of this tail in a quantitative manner has always posed problems, mainly because the standards used for sensitivity factors do not include the tail and in most cases of analysis the tail extends beyond the window used for the narrow scan. Thus to undertake quantification in XPS analysis it is normal to remove a background which is based on the original Shirley algorithm,@footnote 2@ i.e. an integration of the peak lying above background using an integration constant which allows the background to merge with the experimental data at some point close to the peak. A browse through a collection of standard xp spectra of the elements quickly reveals what many of us recognise from experience: That the intensity removed by the Shirley background differs from one element to another. Over the past few years, working with Pr.A.M.Salvi, we have shown that this part of the background structure varies in a systematic manner across a row of the periodic table. In this review we bring together results published in several journals@footnote 2-6@ in an attempt to give a unified account of the progress so far made. It will be shown that the intensity of the background can be distinguished from the Tougaard, extrinsic loss, background and characterised by a single parameter. This 'shape' parameter can be of value in peak fitting, especially when fitting over lapping peaks as occurs with oxide films on metals. There is also an element of chemical state information contained in the peak itself. For example we have shown that when aluminium participates in the formation of an aluminide with one of the 3d transition metals, then the aluminium gains the background imprint typical of the 3d elements. Similar findings occur in the formation of other covalent compounds and in the chemisorption of molecules to transition metal substrates. In conclusion the review will show that the Shirley background, far from being part of the spectrum to be discarded, actually contains information of a secondary nature which can be useful in interpretation of the primary analytical results. @FootnoteText@@footnote 1@S. Tougaard, Applied Surface Science, 100/101, pp 1-10 (1996) @footnote 2@D.A. Shirley, Phys.Rev.B, 5 4709 (1972) @footnote 3@Anna Maria Salvi and James E Castle, J. Elec Spec & Related Phenomena, 94 pp 73-88 (1998) @footnote 4@Anna Maria Salvi and James E Castle, "The intrinsic asymmetry of Photoelectron Peaks: Dependence on Chemical State and Role in Curve Fitting", J. Elec Spec & Related Phenomena, 95 pp 45-56 (1998) @footnote 5@J.E.Castle, S.J.Greaves, M.R. Guascito, and A.M.Salvi, "A New Probe of Bonding States in Intermetallic Compounds" Phil Mag. 79, pp 1109-1129 (1999). @footnote 6@J.E.Castle, A.M.Salvi*, M.R. Guascito, "A Substrate-Related Feature in the Loss Structure of Contamination-C1s" Surface and Interface Analysis, 27, 753 - 760 (1999) @footnote 7@J.E.Castle, H.Chapman-Kpodo, A.Proctor** and A.M.Salvi*"Curve-Fitting in XPS Using Extrinsic and Intrinsic Background Structure" J.Elec.Spec.and Rel Phenomena, 106 pp 65-80 (1999)

9:00am MC-WeM3 Formation of Potentially Protective Oxide-free Phosphate Films On Titanium Characterized by Valence Band X-ray Photoelectron Spectroscopy, J.A. Rotole, Kansas State University; K. Gaskell, Nottingham Trent University, UK; A. Comte, Ecole Nationale Superieure de Chimie de Clemont-Ferrand, France; P.M.A. Sherwood, Kansas State University

This paper reports the results of a continuing study focused on preparing novel surface chemistries on metal surfaces. In this paper we report how it is possible to prepare oxide-free titanium metal surfaces protected by a film consisting of phosphate. The surface is prepared by electrochemical treatment in an anaerobic cell which allows electrochemistry to be conducted on samples located in a vacuum system attached to an X-ray photoelectron spectrometer. When a clean metal surface is subjected to

electrochemical treatment in aqueous orthophosphoric acid an oxide-free phosphate film can be formed on the metal which is stable on subsequent air exposure. Compositional variations were found with potential and other factors. Identical electrochemical treatment of as received titanium foil in atmosphere yielded samples that had a surface consisting largely of oxide. The chemical composition of these surface films was studied by core level and valence band X-ray photoelectron spectroscopy. Valence band photoemission interpreted by band structure calculations was found to be especially effective in understanding subtle differences in surface chemistry, enabling the clear identification of phosphate (being able to distinguish between orthophosphate and metaphosphate films) and its distinction from surface oxide.@footnote 1@ @FootnoteText@ @footnote 1@ This work was funded by the National Science Foundation under grant CHE-9421068.

9:20am MC-WeM4 Chemometric Approaches to the Analysis of Surface Chemical Image Data, K.G. Lloyd, D.J. Walls, G.S. Blackman, N. Tassi, J.P. Wyre, E.I. DuPont de Nemours and Co., Inc. INVITED

ToF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry) provides a mass spectrum from the topmost 10-20 Angstroms of a sample, which is in effect a composite of mass spectra from all species that co-exist at the surface. This makes it difficult to track surface compositional changes in multi-component systems, especially when molecular ions are not observed. In the area of chemical imaging, the generally comparable secondary ion yields from most organic species result in little/no contrast observed in total ion images of organic/polymeric samples. Recent advances in technology now allow us to acquire an entire spectrum at each image pixel. This approach results in a huge amount of data and requires an objective, robust, and automated means of data analysis. For all these reasons, chemometric methods such as Principal Components Analysis (PCA) and Partial Least Squares (PLS) have come to play an important role in surface characterization, not just for ToF-SIMS, but for all the surface chemical imaging techniques. We have had considerable success with the use of chemometric approaches for visualizing chemical contrast in chemical images from ToF-SIMS, Raman, and ESCA data. Our work has focused on how to take advantage of the complementary information content of these data sets. This talk will present examples of how we are using these multivariate statistical techniques today, and how we might expect to use them in the future.

10:00am MC-WeM6 Multivariate Analysis of TOF-SIMS Data of Dodecanethiol SAMs: Detailed Spectral Analysis and Insight Into Fragmentation, D.J. Graham, B.D. Ratner, University of Washington

The analysis of novel engineered surfaces will require detailed, molecular specific characterization methods. The power of multivariate analysis in extracting such detailed information from TOF-SIMS spectra of a time series assembly of dodecanethiol SAMs was studied. PCA analysis of the negative spectra showed a relative increase in the intensity of molecular ion clusters and low mass hydrocarbon fragments (C to C3) with increasing time. This trend was also reflected in the positive data where a relative increase of C to C4 hydrocarbon fragments was seen at longer assembly times. This increase was accompanied by a relative decrease in the intensity of C5 and above hydrocarbon fragments. To assure these trends were not just an artifact of the PCA analysis we plotted the original spectral data from the peaks involved in the above trends. These plots verified that the trends seen in the PCA analysis reflected actual trends in the TOF-SIMS data. This data suggests that as the SAM surface becomes more ordered and crystalline the emission of longer fragments from the thiol chains is reduced relative to the emission of short fragments. Thus PCA is extracting information about the interaction and energetics of the surface. Using the PCA trends, a multivariate ratio (SAMratio) was created. This ratio was applied to a completely different set of thiol SAMs of varying chain length and head group. A correlation was found between the SAMratio and the parachor of the surfaces. Therefore PCA analysis was able to determine real data trends that lead to insight into the TOF-SIMS fragmentation process and a direct correlation with a thermodynamic property of the surface. The ability to extract this type information has the potential to revolutionize TOF-SIMS analysis by unlocking the information within the TOF-SIMS fragmentation pattern that is not accessible from univariate analysis.

10:20am MC-WeM7 Z-dol PFPEs on Magnetic Recording Disks: A PLS Study of TOF-SIMS Spectra, A. Spool, K. Kuboi, R. Waltman, P. Kasai, IBM Corporation

Statistical methods were used to show how variations in the peak intensities in the TOF-SIMS spectra of Z-dol Perfluoropolyether (PFPE)

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lubricant deposited on magnetic recording disks vary with the properties of the lubricant. Partial Least Squares analysis of a large number of spectra successfully modeled variations in lubricant thickness, molecular weight and the ratio of the 2 main repeating units in the Z-dol copolymer. The peaks of most significance (largest absolute regression factor) for each model were then examined to relate fragment structures to the physical property being modeled. This in turn was used to further our understanding@footnote 1,2@ of the spectra themselves. @FootnoteText@ @footnote 1@ A. M. Spool and P. Kasai, Macromolecules 29, 1691 (1996). @footnote 2@ P. H. Kasai and A. M. Spool, J. Phys. Chem. B 102, 7331 (1998).

10:40am MC-WeM8 Exploration of the Time-of-Flight Secondary Ion Mass Spectra of Combinatorially Designed Polyarylates by using a Novel Multivariate Statistical Approach, *B.J. Tyler*, Montana State University; *A. Belu*, Physical Electronics

In this study, a novel multivariate data analysis method has been used to explore relationships in the TOF-SIMS spectra from a series of polyarylates, with well-controlled and systematically varying chemistry. A series of 16 polyarylates was prepared from 4 distinct tyrosine-derived dipheols and 4 aliphatic diacids. This series is a subset of a library of 112 polyarylates described by Brocchini et al. These materials which have well controlled and systematically varying chemistry are ideal for evaluation by surface analysis techniques. The effects of incremental increase in polymer backbone length and polymer side-chain length can be evaluated. SIMS spectra of these polymers have been investigated by Belu, et al. These polymers show a series of peaks which are shifted by a mass characteristic of the particular polyarylate chemistry. Although principal components analysis and other multivariate methods have proved to be a very powerful aid for interpreting SIMS spectra, patterns which are shifted by a mass unit are invisible to these methods. A novel approach to multivariate analysis has been developed which is sensitive to characteristic shifts in the mass spectra rather than solely to peak positions. Details of the multivariate method as well as results for the polyarylate polymer series will be presented. @FootnoteText@ @Footnote 1@Brocchini S, James K, Tangpasuthado V, Kohn J, JACS, 1997; 119(19): 4553-4554 @Footnote 2@Belu A, Brocchini S, Kohn J, Ratner B, Rapid Communications in Mass Spectrometry, in press.

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