## Wednesday Morning, November 17, 2004

Applied Surface Science

Room 210A - Session AS-WeM

#### Chemometric Analysis of Spectral or Image Data; XPS/TOF-SIMS Applications

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

# 8:20am AS-WeM1 Angle-resolved X-ray Photoelectron Imaging of Heterogeneous Polymer Samples, K. Artyushkova, J.E. Fulghum, The University of New Mexico

ARXPS has been widely used for thickness calculations, discerning molecular orientation, and estimating both surface enrichment and concentration gradients. For multicomponent heterogeneous samples not only the average concentration but morphology and chemical heterogeneity are important. In this work we demonstrate the results of combining ARXPS and imaging for analysis of polymer blend samples. Challenges in combining the two approaches include locating the same area for image acquisition at multiple take-off angles, the small depth of focus in imaging mode, and the geometrical transformation of images with changing take-off angle. The conversion of the original photoelectron images to a volume representing the top 3-10 nm of the polymer blend includes principal component analysis, spatial image transformation to correct for geometry or image warping, automatic image registration, mapping images to concentration with the assistance of AR small area spectroscopy, image morphing and visualization. AR images were used to create volumes from the top 3-10 nm of blends of polyvinylchloride (PVC) and polymethylmethacrylate (PMMA) or polystyrene (PS). These volumes allow for the visualization and estimation of the degree of surface segregation and separation of polymer phases. This work has been partially supported by NSF CHE-0113724.

#### 8:40am AS-WeM2 Detection of Small Chemical Changes on Liquid Crystal-Aligning Polymer Surfaces using Multivariate Data Analysis of XPS Spectra, S. Pylypenko, K. Artyushkova, J.E. Fulghum, The University of New Mexico

Ion beam alignment of liquid crystals is one of several non-contact methods under investigation as a substitute for mechanical rubbing. The characterization of Ar+ ion beam modified polymers is required in order to understand the macroscopic and microscopic alignment mechanisms. Polymer alignment layers, including polyimide and polystyrene, were studied using X-ray Photoelectron Spectroscopy (XPS) to characterize chemical changes and the surface anisotropy of the alignment substrate. XPS spectra were acquired from samples before and after bombardment, after exposure to the atmosphere, and after 90 degree rotations. XPS spectra of the polymers are dominated by changes resulting from Ar+ ion beam exposure, but also contain smaller changes related to chemical anisotropy. The effect of surface oxidation resulting from the high reactivity of the polymer surfaces after bombardment also must be taken into consideration when interpreting the spectra. We used multivariate analysis to differentiate between chemical changes from ion beam bombardment and oxidation versus the small changes due to chemical anisotropy created by the ion bombardment. Spectra manipulation, including subtraction, and multivariate analysis using Principal Component Analysis (PCA) and Multivariate Curve Resolution (MCR) allowed us to extract information about small changes due to chemical anisotropy. The anisotropy, and associated liquid crystal alignment, result from selective destruction of the weakest bonds relative to the direction of ion beam bombardment.

#### 9:00am AS-WeM3 Identifying Surface Chemical Changes with XPS Spectral Imaging and Multivariate Statistical Analysis@footnote 1@, D.E. Peebles, J.A. Ohlhausen, K.R. Zavadil, M.R. Keenan, P.G. Kotula, Sandia National Laboratories

Imaging X-ray Photoelectron Spectroscopy (XPS) allows the distribution of elements and chemical states to be mapped across a surface region of interest. Conventional use of XPS mapping involves utilizing images acquired at peak intensities for chemical species of interest with the subtraction of a suitable background image off the peak. Both peak and background image energies need to be determined from a prior spectrum taken from the imaged region to insure optimal energy selection. While this allows differentiation of chemical states, image contrast and resolution may be poor, especially for overlapping spectral peaks. A more complete and definitive picture of the distribution of chemical species across the surface may be obtained by acquiring a series of images over an energy range that covers the peaks of interest. This generates a very large amount of data that must be processed and correlated, generally with some form of multivariate statistical analysis. Many types of multivariate statistical analyses require user input for the number of species present and their general lineshape. Others produce non-physical spectra that may be difficult to interpret. Multivariate statistical analysis methods developed at Sandia National Laboratories facilitate the rapid analysis of the large quantities of data produced by spectral imaging in an efficient manner without user bias or input. The use of these methods for XPS spectral images to detect changes in chemical state will be demonstrated. In particular, examples illustrating the ability of these techniques to resolve overlapping peaks and reveal correlated species will be included. @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.

### 9:20am **AS-WeM4 Algorithm for Improved XPS-Imaging**, *S. Tougaard*, University of Southern Denmark, Denmark

Non-destructive XPS-imaging of surfaces is based on analysis of peak intensities. It is however well known that XPS-quantification from the peak intensity leads to huge uncertainties because the measured intensity depends strongly on the depth distribution of atoms. The problem was basically solved by developing models for the detailed analysis of the energy distribution of emitted electrons leading to algorithms summarized in.@footnote 1@ The validity of these algorithms have been extensively tested experimentally and found to be able to accurately determine both the quantitative amount of atoms as well as their in-depth distribution within the outermost ~ 5-10 nm of surfaces. Practical application of these algorithms has increased after ready to use software packages were made available and they are now used in labs worldwide. These software packages are easy to use but they need operator interaction. They are not well suited for automatic data processing and there is a need for simplified strategies that can be automated and used in e.g. XPS-imaging where the huge amount of data hinders manual data analysis. In this paper we study a very simple algorithm that automatically takes the XPS-peak attenuation effect into account@footnote 2@. The algorithm is less accurate than those in@footnote 1@ but it is substantially more accurate than using peak intensities and it is well suited for automation. It gives the amount of atoms within the outermost ~ 3IMFP with a good accuracy and it gives also a rough estimate for the in-depth profile. In the talk, the validity of the simple algorithm is tested on several experimental systems and the results are compared to analysis of the same samples quantified by more accurate methods. The algorithm seems promising for significant improvements in XPS-imaging. @FootnoteText@ @footnote 1@ S. Tougaard, J. Vac. Sci. Technol. A14, 1415 (1996); see also www.guases.com@footnote 2@ S. Tougaard, J. Vac. Sci. Technol. A21, 1081 (2003).

#### 9:40am AS-WeM5 Chemometric Techniques for Two-way, Three-way and Higher-order Image Data, *J.M. Shaver*, Eigenvector Research, Inc., US; *B.M. Wise*, Eigenvector Research, Inc. INVITED

Historically, analytical instrumentation would measure a single response such as intensity or counts as a function of a single parameter such as incident energy (e.g. a spectrum). When this response is measured for a range of samples, one obtains "two-way" data. Each sample gives a single vector of responses. A wide variety of numerical analysis techniques exist for performing quantitative and qualitative analyses of two-way data. However, an increasing number of instruments measure response as a function of multiple parameters such as position on the sample, incident energy, and energy of response. Add to these the measurement of multiple samples and the data can become quite complex with respect to relationships between parameters. One method of analyzing such data is to focus on only one parameter at a time (sample vs. incident intensity) or, alternatively, to ignore the relationship between parameters and string the data into one long series of responses per sample. An more sophisticated approach arranges the data into a multi-way array which can be analyzed for relationships between controlled parameters as a function of sample. This often allows improved accuracy and specificity and, in some cases, is even easier to analyze because of the interrelationships. This paper will discuss the concept of multi-way data and some of the issues associated with its analysis, with particular note to multi-way spectroscopic images.

#### 10:20am AS-WeM7 Maximum Likelihood Principal Component Analysis of ToF-SIMS Spectral Images, M.R. Keenan, Sandia National Laboratories

Many modern surface analytical instruments are able to acquire huge amounts of data in the form of spectral images. ToF-SIMS, for instance, can easily generate a complete mass spectrum at each point in a 2D or 3D

## Wednesday Morning, November 17, 2004

spatial array. The challenge for the data analyst, then, is to garner the analytically useful information from the overwhelming quantity of raw spectral data. Factor analysis techniques such as Principal Component Analysis (PCA) have proven quite useful in this endeavor. Standard PCA, however, assumes that noise in the data is uniform, that is, that it does not depend on the magnitude of signal. This is clearly not correct for methods that rely on particle counting where the noise is governed by Poisson statistics. In this case, properly accounting for heteroscedasticity is essential to extracting the chemical information into a minimum number of factors while maximally excluding noise. Maximum Likelihood PCA (MLPCA) is one approach to addressing this issue. MLPCA can, in principle, incorporate a separate uncertainty estimate for each individual observation in a data set. This paper will present a MLPCA analysis of a simple and intuitive ToF-SIMS spectral image. The results show that there is a tradeoff between the number of uncertainty parameters included in the model and the quality of each and, in fact, using poor estimates may be worse than doing nothing at all. The best results were obtained by using a low-rank approximation to the noise rather than individual estimates. MLPCA will also be compared with an optimal scaling approach. For the particular example given, the added benefits of MLPCA probably do not outweigh the greatly increased computational demands of the technique. 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.

# 10:40am AS-WeM8 AXSIA Analysis of TOF-SIMS Spectral and Image Series Data@footnote 1@, J.A. Ohlhausen, K.R. Zavadil, R.D. Kilgo, Sandia National Laboratories

AXSIA (Automated eXpert Spectral Image Analysis), a patented multivariate approach invented at Sandia National Laboratories, is used to provide comprehensive analysis of spectral series and spectral image series. We directly compare spectra from many different samples (spectral series) and compare spectral images from different specimens or locations (spectral image series) using this statistical approach. This method of analysis provides full spectral separation of distinct components present within the system of interest. Component variation is expected with fragmentation changes resulting from aging, contamination, concentration, molecular orientation, and chemical reaction. We use spectral series analysis to understand how component variation might be impacted by monolayer deposition and coverage. Spectral series analysis with AXSIA shows promise in extracting a more quantitative determination of the effect of saturation coverage and molecular orientation on fragmentation patterns. We have also been able to process large, complex image datasets containing a number of analysis areas at once. By using a technique of merging multiple datasets into one large dataset, a direct comparison of analysis locations is made. The relative amount of contaminant and substrate species as a function of handling and processing conditions are determined. The effects of processing and handling are readily extracted in this chemical system because all data is processed at once. As a result, the information contained in the component analysis is complete and comprehensive. @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.

# 11:00am AS-WeM9 ToF-SIMS as an Important Tool for Fuel Characterization: A Chemometrics Study, *G. Jiang*, *D. Stone*, *L. Baxter*, Brigham Young University; *B.J. Tyler*, University of Utah; *M.R. Linford*, Brigham Young University

The combustion of coal and biomass provides a significant amount of the energy needs of the world. As expected, there is a series of standardized tests for characterizing these materials. However, these time-consuming analytical methods do not generally provide the chemical information that is necessary to predict and better understand important problems such as NO formation and soot production. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is one of the most powerful surface analytical methods in existence. Here we investigate the possibility of using a single ToF-SIMS analysis to characterize coal and biomass as a replacement for many of the tests that currently need to be performed on each sample. But more importantly we look to ToF-SIMS as a tool that can provide data that is rich in chemical information. To handle the enormous quantities of data that are produced by ToF-SIMS it has become increasingly common to use chemometrics methods such as PCA, PLS, and cluster analysis. Here we report a chemometrics study of ToF-SIMS spectra of a series of coal and

biomass samples. As expected, PCA of ToF-SIMS spectra of coal and biomass show these classes of materials to be distinctly different. In particular, scores and loadings plots of coal and biomass ToF-SIMS spectra show that the coal spectra are dominated by inorganic ions, while the biomass spectra are dominated by organic ions. We also note that data preprocessing has a significant impact on the resulting PCA, where more information appears to be available from the data when normalization and standardization are applied. PLS of biomass data shows excellent agreement between the nitrogen content of these fuels and the ToF-SIMS spectra. In summary, these multivariate analyses help build the case for ToF-SIMS as a useful and powerful tool for fuel analysis.

## 11:20am AS-WeM10 A Chemometrics Analysis of ToF-SIMS Spectra of Monolayers on Scribed Silicon, *L. Yang*, *Y.-Y. Lua*, *G. Jiang*, *M.R. Linford*, Brigham Young University

While chemomechanical modification of silicon with a variety of reagents is now well established, a significant amount of physical characterization remains to be performed on these new monolayers to understand their structures. Time-of-Flight Secondary Ion Mass (ToF-SIMS) was performed on monolayers on scribed silicon derived from 1-alkenes, 1-alkynes, 1holoalkanes, aldehydes and acid chlorides. In order to best analyze the vast quantity of data that is produced by SIMS a chemometrics analysis was performed. Principle component analysis (PCA) proved to be a powerful tool for data compression and information extraction. Nine different PCA analyses were performed, including analyses of i) negative, ii) positive, and iii) combination of the negative and positive spectra, using i) normalized data, ii) normalized and mean-centered data, and iii) normalized and standardized data. If only normalization is performed the first PC loses most of its information content, as it mostly relates to the distance between the spectra (plotted as single points in a hyperspace) and the origin. If both normalization and standardization are performed it is difficult to extract information from the data because too much noise is given equal importance with the data. The positive and negative ion spectra contain complementary information. PCA of negative ion spectra gave a good separation of the monolayers according to the types of adsorbates used in monolayer preparation. PCA of positive ion spectra primarily separated the monolayers according to the number of carbons in their precursor. PCA of the combined positive and negative ion spectra is similar to that of negative spectra. Loadings plots showed the variables that best account for the variability in the data. PCA also indicates the presence of a few outliers in a large set of data, which further shows the usefulness of this method for demonstrating and confirming surface quality. The results of this study are an excellent confirmation of monolayer formation on scribed silicon from a series of different precursor molecules.

#### **Author Index**

#### Bold page numbers indicate presenter

A —
Artyushkova, K.: AS-WeM1, 1; AS-WeM2, 1
B —
Baxter, L.: AS-WeM9, 2
F —
Fulghum, J.E.: AS-WeM1, 1; AS-WeM2, 1
– J —
Jiang, G.: AS-WeM10, 2; AS-WeM9, 2
– K —
Keenan, M.R.: AS-WeM3, 1; AS-WeM7, 1

Kilgo, R.D.: AS-WeM8, 2

Kotula, P.G.: AS-WeM3, 1 — L — Linford, M.R.: AS-WeM10, 2; AS-WeM9, 2 Lua, Y.-Y.: AS-WeM10, 2 — O — Ohlhausen, J.A.: AS-WeM3, 1; AS-WeM8, 2 — P — Peebles, D.E.: AS-WeM3, 1 Pylypenko, S.: AS-WeM3, 1 — S — Shaver, J.M.: AS-WeM5, 1 Stone, D.: AS-WeM9, 2 — T — Tougaard, S.: AS-WeM4, 1 Tyler, B.J.: AS-WeM9, 2 — W — Wise, B.M.: AS-WeM5, 1 — Y — Yang, L.: AS-WeM10, 2 — Z — Zavadil, K.R.: AS-WeM3, 1; AS-WeM8, 2