Thursday Morning, October 21, 2010

Applied Surface Science
Room: Cochiti - Session AS1-ThM

Advanced Automation and Data Processing
Moderator: V. Smentkowski, GE Global Research Center

8:20am AS1-ThM2 Chemical State Thin Film Characterisation by Angle Resolved XPS Using the Maximum Entropy Method, *A.J. Roberts, G. Mishra, K. Macak,* Kratos Analytical Ltd., UK*, C. Moffitt,* Kratos Analytical Inc., UK
The application of thin films with nanometre thickness is being driven by their use in many industries. Angle resolved x-ray photoelectron spectroscopy (ARXPS) is a uniquely placed technique providing non-destructive quantitative chemical state depth distribution of elements in the first few nanometres of a surface.

Acquisition of ARXPS using modern instrumentation is now straight forward but determining the depth distribution of elements and their chemistry is more challenging. One numerical method for the reconstruction of depth profile data from ARXPS is the maximum entropy method (MEM). The precision of the reconstructed depth profile depends both on the noise in the experimental data and on the accuracy of the physical model. Furthermore effects of elastic scattering of the photoelectrons and analyser acceptance angle of the analyser must also be adequately accounted for. The influence of the fitting algorithm on reconstructed depth profiles from ARXPS has recently been reviewed [1] for high-k multilayer materials with emphasis on the importance of prior knowledge and/or constraints to achieve high quality profiles. Work presented here expands on the previous conclusions and explores the effect of data collection conditions such as instrument operating mode, analyser collection angle and signal to noise on the reliability of reconstructed profiles for multilayer thin films and modified surfaces.

[1] T. Conard, K. Macak, G. Mishra, W. Vandervorst IUVSTA-59 Workshop

8:40am AS1-ThM3 Strategies for Multivariate Analysis of Very Large Spectral Images*, M.R. Keenan*, Consultant **INVITED**
The sizes of spectral image data sets, always large, are becoming truly huge with modern spectral imaging techniques. Taking ToF-SIMS as one example, image depth profiling can yield data sets comprising several million individual mass spectra arrayed in three spatial dimensions. Spectral complexity is also increasing, particularly in biological applications where more mass channels and higher spectral resolution are required to separate and identify the species of interest. The tools of multivariate statistical analysis (MVA) have proven valuable aids to interpreting complex, high-dimensional data. Given the realities of huge data sets, however, straightforward application of these techniques strains the computing resources available in the typical analytical laboratory. In this paper, we propose a two-stage strategy for multivariate analysis of very large spectral images. In the extraction phase, we seek to efficiently distill the chemical information contained in the data into a minimum number of components that describe the spatial and spectral characteristics the species making up the sample. Principal Component Analysis (PCA) of data suitably preprocessed to account for non-uniform noise is the maximally parsimonious method for extracting information. Techniques for exploiting characteristics of the raw data, such as sparsity, and approaches to estimating the noise covariance on-the-fly can make order-of-magnitude computational improvements in PCA. Owing to the physically irrelevant constraints imposed on the principal components, however, they are notoriously abstract in appearance and difficult to interpret. In the second, or interpretive, stage of MVA, we will perform rotations or transformations of the principal components that are inspired by physically meaningful sample or spectral features such as component non-negativity, sparsity, independence and simplicity. Abstract factor rotations, such as the Varimax method, are time-honored tools in Factor Analysis, but appear to be underutilized in chemometrics. In this talk, we will discuss a general and rapid method for performing factor rotations based on arbitrary optimization criteria. Besides making a connection between factor rotation and seemingly disparate techniques such as Independent Component Analysis (ICA) and Maximum Autocorrelation Factors (MAF), we will present several novel rotations that have potential use in spectral image analysis. An important point, here, is that the rotations entail relatively low computational cost allowing us to examine our results from multiple points of view with an eye toward find representations that best help us solve the chemical problem at hand.

9:20am AS1-ThM5 Report on the 59th IUVSTA Workshop: Surface Chemical Analysis – Improving Data Interpretation by Multivariate & Informatics Techniques*, J. Tyler*, University of the West Indies, Trinidad and Tobago
The 59th IUVSTA Workshop: Surface Chemical Analysis - Improving Data Interpretation by Multivariate & Informatics Techniques was held at the Salybia Nature Resort in the Republic of Trinidad and Tobago from April 11 -16, 2010. The purpose of the workshop was to provide a forum for presentations and discussions in order to advance the field of Surface Chemical Data Analysis and Interpretation. Thirty-two scientists attended the meeting, including representatives from industry, academia and National Laboratories. The participants ranged from senior scientists to graduate students. Experts in surface science and chemometrics participated alongside those who were relative neophytes in one area or the other. The workshop was organized into 14 sessions, each with two to three formal presentations and an extended discussion period, and a final summary session. Many discussions lasted for more than an hour. During the discussions it was evident that there is no single data analysis method that is ideally suited to all problems and that guidelines are needed to assist analysts in selecting the most appropriate techniques for their objectives. The necessity for appropriate preprocessing of data, including peak selection, dead time correction, normalization and scaling was an oft repeated theme. A variety of approaches to enhance correct chemical interpretation of results were discussed. One full day of the workshop focused on biological applications, highlighting the value of multivariate methods when dealing with chemically and spatially complex samples and the difficulties of handling very large data sets. Although SIMS was a focus of much of the discussion, emerging issues in analysis of imaging XPS, NEXAFS, MALDI and multi-technique data sets were addressed. Key issues that arose during the discussions included the need to create guidelines and best practices, the value of mentoring, and the critical demand for a rapid, easy to use interface between vendor software and advanced data analysis packages. A series of action items were developed to address these critical issues, including creation of a website for exchange of data, software programs and bibliographical information; creation of a blog for continued community discussion; completion of an ISO technical report that would provide guidelines and establish best practices and a request to instrument vendors to improve the transparency and to simplify the interface between their software and data reduction programs. A full report on the conference and progress to date on these action items will be presented.

9:40am AS1-ThM6 Multivariate Analysis of NEXAFS Spectrum Images*, J.A. Ohlhausen, M.T. Brumbach,* Sandia National Laboratories*, C. Jaye, D.A. Fischer,* NIST*, E. Principe, P. Sobol*, Synchrotron Research, Inc.
Multivariate analysis methods have been applied to Near Edge X-ray Absorption Fine Structure (NEXAFS) spectrum images acquired at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratories (BNL). NEXAFS has typically been a large spot technique, but with the new imaging system on U7a at NSLS, spectrum images can now be acquired. These spectrum images can be processed univariately, but many issues confound the analysis. Issues include overlapping peaks, broad spectral features, poor contrast, non-zero backgrounds and unique synchrotron-related data artifacts. We will discuss these issues and their implications to successful multivariate analysis. Strategies for removing non-uniform illumination and time-dependent illumination decay will be shown. Additionally, the energy of secondary electrons can be filtered so that the depth of analysis is varied, leading to depth and spatially-resolved (3D) chemical information. We will demonstrate the multivariate analysis of data acquired by this technique as well.

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