Applied Surface Science
Room: 204 - Session AS-WeA

Developments in Electron Spectroscopies for Non-Ideal Samples 2
Moderator: A. Herrera-Gomez, CINVESTAV-Queretaro, Mexico

2:00pm **AS-WeA1 Albert Nerken Award Lecture - Photocathodes for Future X-ray Light Sources**, ***H.A. Padmore****, Lawrence Berkeley National Laboratory **INVITED**

Synchrotron sources of x-rays have revolutionized many areas of materials science. From the 1st generation synchrotrons of the 1970s to the 3rd generation of storage ring-based machines of today, the brightness has increased by around 6 orders of magnitude. Measurements that were formerly done at the mm spatial scale have become routine at sub 100 nm spatial resolution. New methods such as ptychography are taking us now to nm resolution. Storage rings can be pushed further, and sources with full transverse coherence are planned, increasing the brightness again b y 2 - 3 orders of magnitude. Over the last 10 years, there has been a parallel development of Free Electron Lasers (FELs), that push the peak brightness up again by a further factor of 10^{10} and reduce pulse length to the few fsec range. These machines complement quasi cw synchrotrons and are the tool of choice for studying ultrafast dynamics. I will briefly review some of these historical developments, and then focus on a key enabling technology for MHz repetition rate FELs, the production of ultrafast pulses of electrons from photocathodes. I will review our current work in the synthesis of high efficiency alkali antimonide based cathodes, and cathodes based on non-linear photoemission from plasmonic systems.

2:40pm **AS-WeA3 Monochromatic Ag Lα for XPS – A Practical High Energy X-ray Source**, ***S.J. Coultas****, J.D.P. Counsell, S.J. Hutton, A.J. Roberts, C.J. Blomfield, C. Moffitt, D. Surman*, Kratos Analytical Limited, UK

The concept of high energy X-ray sources for laboratory based XPS analysis has been around for a long time. The often cited work by Yates and West was published thirty years ago [1]. However, it is still rare to find data in the literature recorded using X-ray sources other than Al Kα or Mg Kα. In this paper we attempt to illustrate the usefulness of the Ag Lα source for a variety of sample types.

After Al Kα, Ag Lα is probably the most practical monochromatic source for standard laboratory based XPS instrumentation as it utilises the second order diffraction of the same quartz crystals as used for Al Kα. This allows it to be easily accommodated on a modern spectrometer.

The photon energy of Ag Lα is 2984.2 eV, approximately twice that of Al Kα (1486.6 e). This greater energy leads not only to the excitation of additional, higher binding energy, core lines for some elements (Table 1) but also the possibility of analysis of deeper layers due to the decrease in attenuation length with increasing photoelectron energy [2]. For example, the ineleastic mean free path (IMFP) of C 1s, binding energy 285 eV, using Al Kα X-rays is 3.14 nm at a kinetic energy (KE) 1201 eV, but for Ag Lα this is increased to 5.89 eV at KE 2699 eV [3].

In this work we present examples of sample analysis where the consequences of using a higher energy excitation source have been exploited. Examples of using higher binding energy core lines, such as Si 1s and Hf 3d, are presented together with applications utilising the greater information depth available from the source. We have studied samples using both spectroscopy and imaging and explored the depth dimension by ARXPS and depth profiling.

Table 1: Elements with core line binding energies in the range of Ag Lα X-rays but not Al Kα (*at least one half of doublet)[4]

Core Line	Element
1s	Al Si P S Cl
2s	As - Mo
2p	Br - Ru
3s	Pr - Re
3p*	Sm - Tl
3d*	Tm - Rn

*** Albert Nerken Award Winner**

References

[1] K Yates & RH West, *Surf. Interface Anal*., 1983, **4**, 5

[2] MP Seah & WA Dench, *Surf. Interface Anal*., 1979, **1**, 2

[3] www.nist.gov/srd/nist71.cfm

[4] X-Ray Data Booklet LBNL/PUB-490 Rev.2 Jan 2001

3:00pm **AS-WeA4 Industrial Applications of Auger Electron Spectroscopy (AES) in GE Research and Development Laboratory**, ***H. Piao****, L. Le Tarte,* General Electric Co., *D.F. Paul*, Physical Electronics Inc.

Auger Electron Spectroscopy (AES) is one of the most widely used techniques for quantitative surface analysis. AES is the dominant technique in numerous applications in industries. The advantage of high spatial resolution in AES makes it an attractive technique over XPS in solving new types of problems in a diverse range of technologies that are growing in importance. The presentation gives an emphasis on unique advances in surface analysis using AES, including the application of TEM specimen preparation techniques (FIB, microtome and ion-milling). We also demonstrate high energy resolution applications for chemical states analysis by the concept of the sample biasing method [1].

Keywords: AES, energy resolution, chemical states

[1] D.S. Watson, P.E. Larson, D.F. Paul and R.E. Negri, *Surf. Interface Anal*. 44 (2012) 121.

4:00pm **AS-WeA7 Developing Electron Spectroscopy to Meet the Characterization Needs of Modern Materials – Past, Present and Future Challenges**, ***D.R. Baer***, Pacific Northwest National Laboratory **INVITED**

As surface analytical methods, Auger electron and x-ray photoelectron spectroscopies (AES and XPS) are now approximately fifty years old and both are in wide use. Based on the rapidly growing number of publications, XPS has become the most widely applied method for surface chemical analysis. Although analysis is now mostly routine and quantitative as applied to many types of samples, it has taken considerable effort by many in the research and vendor communities to establish the instrument quality and implement new technologies and to establish the fundamental understanding and relevant physical data needed to develop the accurate approaches to analysis that are now available. However, many modern materials have significant characterization requirements that extend beyond those available using many of the standard measurement and analysis approaches in routine use and as supplied by instrument vendors. In this talk we will look at the types of advances that have taken place over the past four decades and explore some of the issues that were identified that needed to be addressed along the way. Although many of these are now transparent to instrument users, some of them highlight the types of unexpected challenges that can arise when careful analysis is required. The roles that AES, XPS and other methods may play in meeting the significant analysis challenges presented by a new generations of organic, composite and other nanomaterials will be discussed. Among the issues that need to be considered are: sample preparation, mounting and analysis damage; *in situ* and time-dependent analysis; three dimensional structure information; rapid imaging; multimodal and functional characterization; coating uniformity and thickness; surface functionality; analysis speed and cost, and the nature and presence of very minor amounts of contamination. Many of these issues are not new, but the advanced materials now capable of being synthesized exaggerate some of the challenges and raise additional problems still to be addressed.

This talk has evolved from research programs, research conducted as part of the EMSL User Program (www.EMSL.PNL.gov), and interactions with colleagues from around the world. Portions of this work were performed using EMSL, a national scientific user facility sponsored by the Department of Energy's (DOE) Office of Biological and Environmental Research (BER) and located at PNNL. Aspects of the work have been supported by the DOE's Offices of Basic Energy Science (BES) and Biological and Environmental Research (BER) and the NIEHS under Center grant U19 ES019544.

4:40pm **AS-WeA9 Quantifying the Oxidation of Artificially Aged Elastomers with Multivariate Analysis and Imaging NEXAFS**, ***J.A. Ohlhausen****, M.H. Van Benthem, M.C. Celina*, Sandia National Laboratories

Elastomers made of organic polymers are used in forms such as O-rings, gaskets and electrical wire insulation. Changes in oxidation can lead to significant performance changes as mechanical properties are affected; therefore it is important to be able to directly measure oxidation of these materials. Elastomers have been found to exhibit diffusion limited oxidation whereby the edges are preferentially oxidized over the interior of the part.

Much work has been done to characterize ideal elastomer systems; that is, elastomers with no fillers. Fillers, such as oxides and carbon black, confound most chemical analyses. While studies with non-filled elastomers reveal much about the chemistry and mechanical properties in an aged state, the measurement of the oxidation in "real" systems has often involved modulus profiling but much less chemical analyses. We are developing a method that promises to be effective for measuring the oxidation of filled polymer systems based on intrinsic chemical signatures.

Imaging Near Edge X-ray Absorption Fine Structure (NEXAFS) has been found to be a technique that overcomes the major limitations encountered in filled systems. Located at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratories (BNL), imaging NEXAFS is uniquely capable of measuring the local bonding of elements over large length scales. Thus, the oxidation of these polymers can be directly measured using this technique. We are developing the methods to acquire and process data from samples, ultimately providing a direct chemical measure of oxidation.

In this talk, the results from multivariate analysis of the data are used to calculate oxidation. Specific materials, aging conditions, sample preparation, data acquisition, multivariate analysis and results will be discussed.

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5:00pm **AS-WeA10 Quantitative Characterization of Corrosion Oxides on Metal Alloy Surfaces Exposed to High Temperature Water**, ***M.C. Burrell**, J.T. Orr, T.K. Nolan, M.J. LeClair*, Bechtel Marine Propulsion Corporation

Corrosion of metal alloys in high temperature (~500 ^{o}F) water results in the formation of a retained oxide film and the preferential release of metal ions into solution. Quantification of the composition and mass of the retained oxide is required to determine the amount of base alloy consumed, and the identity and quantity of released metal ions. We have characterized the oxide formed on a series of steels, nickel-based alloys, and a cobalt-chromium alloy (Stellite-6B) using a combination of surface analysis, microscopy, and gravimetric methods. These oxide films range from a few tens of angstroms up to several microns in thickness. Electron Spectroscopy for Chemical Analysis (ESCA) depth profiling provides a measure of the relative proportion of metal ions in the oxide film and changes in near-surface composition of the metal; oxide film mass is ideally determined gravimetrically using a chemical dissolution method. In the case of the thin, resistant oxide formed on Stellite, the gravimetric approach was not satisfactory, and the oxide thickness was determined using electron microscopy. This presentation will describe the challenges encountered in the characterization of these complex surfaces, and some general trends in the corrosion behavior as related to alloy composition and surface finish.

5:20pm **AS-WeA11 Surface Preparation for Multitechnique Surface Analyses**, ***A.E. Wright**, P. Mack, T.S. Nunney, A. Bushell*, Thermo Fisher Scientific, UK

Surface analysis using multiple techniques is becoming increasingly common in materials characterisation, where the desire for more detailed chemical and structural information is complemented by increasing functionality and automation in instrumentation. It is now often possible to use a single instrument to analyse a sample using four or more techniques in quick succession.

X-ray Photoelectron Spectroscopy (XPS) has become routine in many laboratories, while related techniques such as Auger Electron Spectroscopy (AES), Ultraviolet Photoelectron Spectroscopy (UPS), Ion Scattering Spectroscopy (ISS) and Reflected Electron Energy Loss Spectroscopy (REELS) are being used more frequently to supplement XPS analyses.

Any sample that has been exposed to the ambient environment will typically have a thin (1-2 nm or more) covering of hydrocarbons and other contaminants, and may also have oxidised, hydrated or undergone other reactions. These surface deposits can have a significant effect on the results of surface analytical techniques.

The aforementioned techniques can provide a wealth of complementary information from the surface and near-surface regions of a material, but they have differing susceptibilities to the common surface modifications and contaminants. This presentation evaluates samples including polymers, metals and semiconductors, and examines methods of overcoming the contamination issues with particular focus on the use of monatomic and gas cluster ion beams for surface cleaning.

5:40pm **AS-WeA12 Interface Analysis of ALD Grown Oxides using Tunable HAXPES**, ***J. Church**, J. Krajewski, R. Opila,* University of Delaware*, C. Weiland*, National Institute of Standards and Technology (NIST)

The roadmap for the development electronic device world follows Moore's law. New challenges appear at with each node. Presently there is a need to find effective ways to characterize a few monolayers of material. In this study, Atomic Layer Deposition (ALD) thin films of ZrO_2 and Nb_2O_5 films have been studied using high-energy synchrotron-based x-ray photoemission spectroscopy, performed at the NIST beamline at the National Synchrotron Light Source. ALD permits precise control of oxide composition, thickness, and coverage. As a result, thin high dielectric constant materials, which are routinely deposited by ALD, are seeing more applications. Given the unique beam energy tuning ability of synchrotron based sources the x-rays are able to effectively probe the interface of ZrO_2 and Nb_2O_5 layers with their respective substrates. Binding energy shifts associated with the chemical environment at the interface of up to 1.4 eV and 1.1 eV for the ZrO_2 and Nb_2O_5films respectively have been found. These energy shifts suggest significant charge transfer at the interface between the high-k oxide and the Si. In addition, the composition and chemistry of the films as a function of thickness has been determined non-destructively by converting a series of spectra taken with different incident x-ray energies (and simultaneously, different photoelectron sample depths) to depth profiles using Bayesian analyses.

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