Tuesday Morning, October 30, 2012

Applied Surface Science
Room: 20 - Session AS+BI-TuM

Practical Surface Analysis

Moderator: A. Belu, Medtronic, Inc., D.L. Pugmire, Los Alamos National Laboratory

8:00am **AS+BI-TuM1 Clinical Application of Surface Analysis Technologies – Needs, Requirements and Challenges**, ***J. Schnekenburger***, Muenster University, Germany **INVITED**

Surface analysis technologies offer tremendous applications in clinical fields. The interface of cells and materials is a crucial determinant for implant integration, artificial organ regeneration and stem cell differentiation. Cells are highly sensitive not only to chemical but also to structural determinants of their environment. Material softness, roughness and distance of adhesion points are known factors for adhesion, differentiation and the maintenance of cell function. The characterization of cell environments and surfaces for advanced cell culture by surface analysis technologies is a key element of the successful generation of bioimplantable materials and tissue regeneration.

Dental implants and liver regeneration are high impact examples for surface analysis needs. Dental implants should have a structure and chemical composition which facilitates osteoblast adhesion and bone development but impairs microbial growth and adhesion. Different implants were characterized and cell adhesion presented. The regeneration of functional liver cells from mesenchymal stem cells would allow the replacement of donor organs by cell implants. Stem cell differentiation not only requires genetic reprogramming and soluble factors but also a three dimensional environment with key elements of mature hepatocyte surrounding. These surface structures need to be identified and transferred in tissue culture dishes.

The analysis of cells and tissues as materials is challenging. The clinical environment requires technology application processes different from material science. Clinical routine analysis is cost driven and performed by technicians or MDs without deeper technical training. Expert personnel are available only in high throughput clinical centers. Also research is based on understanding the molecular determinants like DNA and proteins rather than material aspects. Furthermore cells and tissues need preparation since biological material can not be measured in high vacuum. The preparation like chemical fixation limits the analysis to specific time points of biological processes and may alter the samples compared to the original state. The combination of technologies like mass spectrometry or scanning electron microscopy with atomic force microscopy or digital holography allows the analysis of preparation artifacts and the generation of reliable data.

Overcoming the current restrictions surface analysis technologies have the potential to replace the biomedical gold standard light microscopy and fluorescence microscopy in the high resolution and three dimensional structural and chemical analysis of biological samples.

8:40am **AS+BI-TuM3 The Application of XPS to the Study of Protein Lyophilizates**, ***S.J. Coultas***, *J.D.P. Counsell, A.J. Roberts, S.J. Hutton, C.J. Blomfield,* Kratos Analytical Ltd, UK, *R. Geidobler, G. Winter*, Ludwig-Maximilians-University, Germany

Long term storage of proteins is most often achieved by freeze drying (lyophilization). For this to be successful it is essential that the process retains the stability and biological activity of the protein. Despite its widespread use there are still problems associated with the process, not least the aggregation of the protein at the ice/liquid interface which develops during the freezing stage. To overcome this problem excipients are commonly used to ease the stresses at this interface and stabilise the protein. Polysorbates are commonly used for this purpose but there has been recent interest in using other excipients.

X-ray photoelectron spectroscopy (XPS) is ideally suited to the study of these materials due to its surface sensitivity (1-10 nm) and the quantitative nature of the data.

In this study we use XPS to investigate the protein stabilisation mechanism in lyophilizates produced using different excipients. We show there to be clear differences in the surface chemistry of the resultant lyophilizates. We also investigate the effect of temperature on the protein surface chemistry and stability.

9:00am **AS+BI-TuM4 Characterization of Real-World Surfaces and Interfaces of Devices in the Biomedical Industry**, ***W. Theilacker***, *A. Belu, L. Lohstreter, L. LaGoo*, Corporate Technology and Innovation, Medtronic, Inc.

This presentation will highlight the use of surface analysis methods for the characterization of medical devices. Examples will be presented to demonstrate a range of practical applications in solving industrial problems. A multi-technique approach is used to better understand issues of cleanliness, adhesion, and intentional surface modification with regards to pacemakers, leads, and other cardiovascular devices. Oftentimes the samples provided are non-ideal for surface sensitive techniques, e.g. they are large, non-flat, and have been handled, or have been in contact with other materials. This presentation will also address approaches for characterization of real-world, non-ideal samples. The surface is an important zone as it is the interface between a material of interest and its environment. Knowledge of interface chemistry is critical for understanding how a biomaterial or drug delivery system will interact with the biological environment of the body. For other materials, particularly those that are employed in the manufacture of medical devices, evaluation of the surface is important to further understand issues with welding, adhesion, contamination, discoloration, etc. Many techniques may be utilized in order to gain a comprehensive understanding of surface morphology and chemistry, including traditional techniques such as SEM-EDS (scanning electron microscopy energy dispersive spectroscopy), IR (infrared) spectroscopy, along with other techniques such as confocal Raman microscopy, interferometry, ellipsometry, XPS (x-ray photoelectron spectroscopy), and TOF-SIMS (time-of-flight secondary ion mass spectrometry). A comparison of the techniques will be made to help elucidate which method or methods are best for specific problems. Further, the power of and the problems with data acquisition and interpretation will be highlighted with regards to each technique.

9:20am **AS+BI-TuM5 Ageing Processes Occurring on Nanoscaled Aminated Surfaces as Observed by ToF-SIMS/PCA, NEXAFS Spectroscopy and XPS**, ***W.E.S. Unger***, BAM Federal Inst. for Materials Res. and Testing, Germany, *H. Min*, BAM Federal Inst. for Materials Res. and Testing and KAIST Korea, *S. Swaraj*, BAM Federal Inst. for Materials Res. and Testing and Soleil Synchrotron France, *P.-L. Girard-Lauriault*, BAM Federal Inst. for Materials Res. and Testing and McGill Univ. Toronto, *A. Lippitz*, BAM Federal Inst. for Materials Res. and Testing, Germany

Ultrathin organic surfaces covered by amines as coupling sites are often used in recent technologies as biosensing, adhesion in composite materials and layer-by-layer deposition of nano structures on self-assembled monolayer platforms. Ageing processes occurring with those aminated surfaces have to be regularly controlled in order to guarantee their functionality in applications.

We used a combined XPS, NEXAFS spectroscopy and ToF-SIMS/PCA approach to follow ageing of different kinds of amino-terminated surfaces stored on ambient air up to ~1 year. Test samples have been prepared as (1) aliphatic and aromatic aminosilanes on glass slides, (2) aminothiols prepared as self assembled monolayers and (3) by different plasma polymerization technologies (low pressure and atmospheric pressure DBD plasma polymerization).

The observation common to all investigated films is that the ageing process ends with a formation of amides which has been clearly proven by NEXAFS N K-edge spectra and PCA of ToF-SIMS data. However the kinetics of the ageing processes, the decay of amines, has been found to be rather different for the different kinds of samples investigated. The susceptibility of plasma deposited films is much higher the due to the radicals inherently produced by the deposition technique. Furthermore storage conditions have been found at which the decay of amines in course of ageing can be suppressed to some extent.

9:40am **AS+BI-TuM6 Signature Discovery in Explosives and Bioagents using Imaging Mass Spectrometry**, ***C.M. Mahoney***, Pacific Northwest National Laboratory

Recent terrorist attacks, both in the US and abroad, have indicated that significant improvements in intelligence operations are required for adequate prevention and prosecution of terrorist acts. This includes the ability to accurately and rapidly attribute pre-detonated and post-detonated explosive devices and/or other weapons-based material to a particular source, and/or region of the world. Surface mass spectrometry methods have the potential to greatly advance the field of forensics science, allowing for simultaneous elemental, isotopic and molecular imaging on a sub-micron to nano-scale range, with superior chemical specificity and

sensitivity. With recent advancements in the field of surface mass spectrometry, the versatility of these methods has increased dramatically, allowing for the direct analysis of samples at atmospheric pressure (e.g. Desorption ElectroSpray Ionization or DESI). The potential for 3-D molecular analysis in soft samples with depth resolutions on the order of 5 nm has also been realized with advent of the gas cluster ion beam (GCIB) source. Finally substantial improvements in the mass resolving power (by at least a factor of 10) has been observed when employing FT-MS mass spectrometers, allowing for even greater improvements in the chemical specificity. Here we describe our efforts to develop a suite of advanced mass spectral analysis and imaging techniques for the characterization and attribution of plastic explosives and other complex explosive mixtures from around the world. We will also provide initial feasibility studies for the characterization and differentiation of biological agents based on their unique molecular fingerprints. With the development of these very powerful "chemical signature microscopes" it is expected that significant advancements will be made in the field of forensics, both on the home front, and abroad.

10:40am **AS+BI-TuM9 Topography and Field Effects in the Inner Side of Micro via Hole using ToF-SIMS**, ***J.C. Lee***, *Y.K. Kyoung, I.Y. Song,* Samsung Advanced Institute of Technology, Republic of Korea, *S. Iida,* Ulvac Phi, Japan

Surface topography is often important role in the functionality and activity of electronic devices including MEMS, composite materials, catalysts, sensors, biomedical, and packaging of semiconductor devices. Especially, trench structure such as via hole or etched pattern is one of the important processes in the through silicon via or ball grid array. If there is contaminated on the wall or bottom of via hole, it may cause contact failure between integrated circuits and printed circuit board (PCB) because of increasing contact resistance. For the recent decade, many research activities are focused on the quantitative analyses of topographic samples using TOF-SIMS. However, the most of results were focused on the nanowire, nano particle, and etched surface, it is relatively rarely dealt with the trench shape sample. It is not easy to characterize the contaminant level of ~ppm or less on the bottom of trench shape sample such as via hole. It is well known that a ToF-SIMS is one of powerful tools to analyze organic contaminants. However there are some limitations to apply it to the trench shape sample because of high sample bias voltage and short focal length of emersion lens of ToF-SIMS analyzer. If we want to characterize contaminants on the bottom of via hole using a ToF-SIMS, the side wall of via hole should be removed by mechanical treatments. In this study, we aim to establish an optimized method that is able to characterize the bottom and wall of via hole of BGA using ToF-SIMS without any mechanical or chemical treatments. This is performed by combining ToF-SIMS experiments using via hole systems with computer modeling using SIMION.

For this study, trench structure samples with the diameter of 90μm and width of 90μm were used for TOF-SIMS imaging. Via holes were fabricated by laser drilling method. Samples were mounted on the sample holders which were specially designed with tilted angles of 15, 28, and 40 degrees surfaces for this experiment. Secondary ion trajectory and potential contour were calculated using SIMION for 0, 15, 28, 40 degree tilted samples for understanding the angle dependence of field effects.

According to the simulation results, secondary ions ejected from near corner between wall and bottom of via hole are aimed to diagonal direction due to Coulomb repulsive force between secondary ions and wall of via hole. When specially designed 40 degree tilted angle sample holder which is based on simulation result is used, the bottom and wall of via hole of BGA can be fully characterized using ToF-SIMS without any mechanical treatment.

11:00am **AS+BI-TuM10 Using XPS to Probe the Surface Chemistry of Ionic Liquids**, ***J.D.P. Counsell***, *S.J. Coultas, A.J. Roberts, S.J. Hutton, C.J. Blomfield,* Kratos Analytical Ltd., UK

Ionic liquids have attracted much attention due to their possible "green chemistry" applications. Due to the recent use of ionic liquids as corrosion resistant thin-films, it has become important to fully understand the complex nature of their surface environments.

A series of commercially available ionic liquids (e.g. [BMIM][PF_6]) were studied and characterised using x-ray photoelectron spectroscopy. Angle-resolved experiments indicate an increased concentration of the organic cation in the liquid's surface. The surface composition becomes enriched with contributions from the linear alkyl substituent of the cation which is significantly greater than that expected from the nominal stoichiometry. A maximum entropy method algorithm was used to build an accurate structure of the surface and near-surface region

We also explore the possibilities of using ionic liquids as potential new reference standards. They present the opportunity to offer a clean reference surface without the need for ion sputtering and present a number of core level peaks for spectrometer energy scale and transmission function calibration and validation.

11:20am **AS+BI-TuM11 XPS Profiling and Work Function Mapping of a Damaged Solar Cell**, ***B. Strohmeier***, Thermo Fisher Scientific, *P. Mack, T.S. Nunney, J. Wolstenholme,* Thermo Fisher Scientific, UK

In many areas of materials technology, it is important to control both the chemical composition and the electrical properties of the material. One example of this need is in the manufacturing of solar cells. In this case, the solar cell is based on a thin film of CIGS (Cu (In, Ga) Se2). The full structure of the device includes an upper electrode containing indium tin oxide (ITO), zinc oxide, and cadmium sulfide. The whole structure is separated from a steel substrate using layers of molybdenum and chromium.

It has been demonstrated previously that X-ray Photoelectron Spectroscopy (XPS) is the ideal technique for characterizing the compositional depth profiles of CIGS solar cells, similar to the one described above. Using XPS it is possible to measure elemental composition gradients in the CIGS layers (allowing engineers to tune the band gap of the device) and also to investigate chemistry at interfacial layers. XPS can also be used to measure another very important parameter of solar cells, i.e. the work function. This measurement relies upon the spectrometer being accurately calibrated and the photon energy being accurately known. On a modern XPS instrument, internal standard samples (copper, silver, and gold) may be used to automatically calibrate the XPS binding energy scale. The photon energy can be checked by measuring the position of an X-ray induced Auger peak on the binding energy scale and adding it to the known kinetic energy for that peak in the Auger spectrum.

This work demonstrates the use of XPS to characterize a damaged solar cell, using depth profiling to identify the delamination zone in the solar cell stack. The surface of the delaminated cell has also been mapped for elemental and work function information.

11:40am **AS+BI-TuM12 Application of XPS Imaging Analysis in Understanding of Interfacial Delamination and Related Problems**, ***H. Piao***, General Electric Global Research Center, *N. Fairley,* Casa Software Ltd, UK, *J. Walton,* The University of Manchester, UK

The recent development of X-ray Photoelectron Spectroscopy (XPS) instrumentation with near-micron spatial resolution has advanced the capability of elemental and chemical state imaging. This work extends the application of imaging XPS to the analysis of real world samples. The presentation also focuses on description of radiation damage of polymers encountered in XPS imaging analysis. The imaging analysis can cause extensive damage to polymers since the acquisition time for creating datasets can be excessive. Understanding of radiation damage in polymers is necessary for successful and validated application of XPS spectromicroscopy.

Keywords: XPS, chemical states, imaging, delamination.

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