Tuesday Afternoon, November 5, 2002

Applied Surface Science Room: C-106 - Session AS-TuA

Imaging in Surface Analysis

Moderator: C.S. Fadley, Lawrence Berkeley National Laboratory

2:00pm AS-TuA1 Using Gold Liquid Metal Ion Sources for Imaging ToF-SIMS, A.V. Walker, N. Winograd, Pennsylvania State University

Molecule-specific imaging TOF-SIMS experiments require the highest possible sensitivity in order to achieve the spatial resolution normally associated with the ion probe. For example, Ga+ ion beams can be focused to less than 100 nm in diameter. However since there are only ~104 molecules per layer and Ga+ ions have a low ionization efficiency, the maximum possible count rate per pixel is extremely small. Previous studies have suggested that sources other than Ga+ produce molecular ions and fragments with higher efficiency, e.g. In+. Gold has also been shown to be an effective source, particularly since it is possible to generate Au++, Au+ and Au2+ beams. Yield enhancements of several orders of magnitude have been reported, although the source was not used in an imaging modality. Here, we examine the prospects for routine use of Au LMIG sources for TOF-SIMS imaging. We employ Au-Si or Au-Ge eutectics to allow the metal to be melted around the tip at a temperature low enough to prevent gold evaporation. Currently, the tips have a lifetime in excess of 1500 amphours. Mass selection is achieved using a double blanking system which allows pulsing and mass selection. The probe size for each of the three gold species is < 300 nm. The performance of this tip will be compared against In and Ga sources for a number of standard materials including Irganox, phenylalanine and several long chain alkanethiols adsorbed on gold. In general, we find the yield of Au is enhanced by up to an order of magnitude over Ga. Of special interest is the fact that Au++ ions exhibit the largest enhancement in many cases, and that Au2+ ions do not yield significant advantage over Au+ ions.

¹H. H. Anderson, A. Brunelle, S. Della-Negra, J. Depauw, D. Jacquet, Y. LeBeyec, J. Chaumont, H. Bernas, Phys. Rev. Letts., 80 (1998) 5433; B. Hagenhoff, R. Kersing, D. Rading, S. Kayser, and E. Niehuis, SIMS XII, (1999) 833.

2:20pm AS-TuA2 Molecular Imaging Using Atomic and Molecular Primary Ions, F. Kollmer, R. Moellers, D. Rading, ION-TOF GmbH, Germany, R. Kersting, TASCON GmbH, Germany, E. Niehuis, ION-TOF GmbH, Germany

The secondary ion yield Y of organic materials increases considerably with the mass of the primary ion. A further yield enhancement can be achieved when changing from atomic to polyatomic primary ions. As the corresponding increase in damage cross section σ is much smaller, the ion formation efficiency E:= Y/σ also increases significantly. The efficiency E not only determines the achievable detection limits in surface spectrometry but also influences the useful lateral resolution Δl in organic imaging via Δl $(1/E)^{A^{1/2}}$. In order to investigate the influence of the primary ion bombardment conditions in imaging of real world samples we applied both monoatomic as well as polyatomic primary ions including Ga⁺, In⁺, Au₁⁺, Au₂⁺ and Au₃⁺. The application of a Au LMIS combines capabilities such as high brightness and high lateral resolution with the advantages of molecular primary ion bombardment. The investigated samples consisted of various thick organic materials with analyte molecules in the mass range > 500 u. The results confirm the dependence of the useful lateral resolution on E and show that imaging of organic materials can best be performed with polyatomic primary ion bombardment. If monoatomic bombardment is used high mass ions are preferable compared to low mass ions. Enhancement factors (E compared to $E_{\epsilon a}$) for polyatomic primary ions reach several orders of magnitude whereas at maximum an enhancement factor of 10 can be achieved with monoatomic primary ions.

2:40pm **AS-TuA3 Topographic Effects in SIMS Imaging**, *S. Rangarajan*, *B.J. Tyler*, University of Utah

One of the most notable of these challenges in TOF-SIMS imaging is differentiating between chemical and topographical effects. The intensity of ion signals depends not only on the surface composition but also upon the surface height and inclination (topography) and the material beneath the surface (matrix). In many cases, the intensity variations due to the structure of the sample can obscure features associated with surface chemistry. Images of surfaces with strong topographic features, including fibers and spherical particles have been presented. Topographic effects include the influences of the height of topographic features, the incident angle between the beam and the surface and variations in the electric field associated with topographic features. We have explored the influence of these topographic features on the absolute and relative ion intensities on conducting and insulating surfaces. Data from both TRIFT and reflectron systems will be presented. When images are generated by rastering the ion beam, topography can cause severe distortions in the image. Additional, particles can create field lines that result in repressed ion emission causing a halo surrounding the particles. Typically, researchers have assumed that topography effects only the absolute intensity of ions but will not significantly alter the relative intensity of peaks in the spectrum. Our results suggest that this assumption is incorrect in many cases. Several data processing methods have been used to compensate for topographic effects in images and there effectiveness will be discussed. Multivariate statistics can help reduce some but not all of these effects on the images. Results will be presented using principle components analysis and mixture models to process images with confounding chemical and topographical features.

3:00pm **AS-TuA4 Towards Quantitative Chemical State XPS Imaging**, *C.J. Blomfield*, *S. Page*, *A.J. Roberts*, *S.J. Hutton*, Kratos Analytical Ltd, UK

XPS imaging is an established method for determining the qulitative lateral distribution of chemical species across a sample surface. Early methodologies for this technique involved acquiring XPS maps, where a virtual probe or X-ray spot was scanned across a sample surface and an image built up pixel by pixel as the analysis point was moved across the sample. Other methods involved the paralell detection over a predefined field of view in one specific binding energy range. Improvements in detector and instrument design in general have lead to the development of truly quantitative pulse counting methods which can give high lateral resolution XPS images with quantitative intensities. This paper describes the issues which must be adressed and the applications which could benefit from a quantitative chemical state imaging technique.

3:20pm AS-TuA5 Analysis Area and Sample Area Viewed by the Analyzer in a Scanning Auger Microscope, C.J. Powell, S.A. Wight, J.T. Armstrong, National Institute of Standards and Technology

The lateral resolution, $\delta r,$ is a critical parameter in a scanning Auger microscope (SAM) since it is a measure of the distinguishability of small objects. For quantitative interpretations of measured Auger signals, however, it is necessary to consider also the analysis area (the area from which all or a defined percentage of the detected signal originates). We report results of model calculations (based on the work of Cazaux¹) that show how the analysis area depends on material parameters associated with backscattered electrons in a SAM. These results are compared with measurements of signal changes as the incident beam in a commercial SAM is scanned across a chemical edge consisting of Cr/CrO2 on indium-tinoxide. As the beam voltage is increased from 5 kV to 20 kV, the effects of backscattering on the analysis area become more pronounced, in general agreement with the calculations. These results indicate that the analysis area can be much greater than $\pi(\delta r)^2$. In addition, we report on measurements of the sample area viewed by the analyzer in the SAM for different electron energies and different analyzer operating conditions. Changes in the sample area viewed by the analyzer as a function of electron energy need to be carefully considered in SAM measurements with different rastered areas.

¹J. Cazaux, Surf. Interface Anal. 14, 354 (1989).

3:40pm AS-TuA6 Materials Characterization using High Spatial Resolution XPS: Multi-technique, Multi-variate, Multi-collaborator Analyses, J.E. Fulghum, University of New Mexico INVITED

Recent instrumentation developments have improved spatial resolution and decreased acquisition times in x-ray photoelectron spectroscopy (XPS). Rapid image acquisition has transformed laboratory XPS imaging from a novelty to an increasingly routine analysis method for surface chemical characterization on the scale of microns. The combination of high spatial and high energy resolution XPS enhances analysis of heterogeneous samples ranging from microelectronic materials to fossils. This enhanced chemical characterization of heterogeneous samples comes at the cost of increasing complexity in the XPS data sets acquired. Spectra-from-images data sets, and imaging series, can produce complex data structures that are not readily interpreted by visual inspection alone. A variety of multi-variate analysis methods can be utilized to facilitate analysis of multi-dimensional data sets, and several examples will be shown. Conclusions based on visual inspection versus principal components analysis will be discussed. New opportunities for multi-technique correlations also arise from the improved spatial resolution and decreased acquisition times. A variety of techniques, including FTIR, AFM and confocal microscopy have fields-of-view which are comparable to imaging XPS, making correlative analyses possible. Data

from multi-component polymer samples will be used to demonstrate the direct correlation of XPS images with other imaging methods. This work has been partially supported by NSF ALCOM (DMR89-20147) and NSF CHE-0113724.

4:20pm AS-TuA8 Nano-XAS and Nano-XPS: Energy-discriminating Imaging Utilizing a PEEM Lens Combined with Retarding or Dispersive Electron Energy Filters, M. Merkel, M. Escher, J. Settemeyer, M. Schicketanz, T. Unger, FOCUS GmbH, Germany, D. Funnemann, J. Westermann, B. Krömker, OMICRON GmbH, Germany, Ch. Ziethen, A. Oelsner, P. Bernhard, F. Wegelin, A. Krasyuk, G. Schönhense, Johannes Gutenberg Universität, Germany

The strong gradient in the field of nanotechnology and materials research calls for surface imaging techniques with nanoscopic lateral resolution and intrinsic spectroscopic information. We will present our recent activities in this field. We have already reported on the combination of a laboratory Xray source with an energy filtered bolt-on photoemission electron microscope (PEEM) optics.¹ Spectroscopic information with sub-micron lateral resolution was possible, however imaging at certain spectroscopic features failed due to the lack of excitation intensity. Recently, this development received strong impetus from novel technical achievements. For example, micro technology delivers new solutions in terms of electron optical components with critical dimensions. Highly brilliant synchrotron beamlines deliver the needed excitation intensity. Finally, state of the art ray tracing and a three dimensional computer aided design is capable of delivering optimised technical solutions. Two approaches with their actual results will be shown in comparison: PEEM imaging combined both with an energy dispersive analyser and with the most advanced RFA type imaging energy filter. The latest milestone results of dedicated research projects will be reported, showing the present limits of Nano-XAS (X-ray absorption spectroscopy) and Nano-XPS (X-ray photoelectron spectroscopy). Until now, we achieved about 20nm lateral resolution using the XAS imaging mode. Using XPS we got about 140 nm resolution. These methods also provide well differentiated spectra drawn from sample areas near the resolution limit. The best energy resolution of both methods is currently about 0.1 eV. Part of the work was funded by BMBF, Germany, through grants FKZ-No: 13N7864, 13N7887 and 13N7863.

¹ M.Merkel, M. Escher, J. Settemeyer, D. Funnemann, A. Oelsner, Ch. Ziethen, O. Schmidt, M. Klais und G. Schönhense, Surface Science 480 (2001), 196-202.

4:40pm **AS-TuA9 Imaging Thin Oxide-Covered Metal Lines with the Photoelectron Emission Microscope***, *V.W. Ballarotto*, *K. Siegrist, M. Breban, E.D. Williams*, University of Maryland

The contrast mechanisms in photoelectron emission microscopy (PEEM) are significantly different than those in secondary electron microscopy (SEM), and thus PEEM may serve as a complementary tool to SEM in analytical applications to semiconductor device characterization. As part of an on-going study to quantify PEEM imaging response^{1,2} we have investigated imaging of metal lines buried under thin layers of silicon dioxide, including the effect of an electrical bias applied to the lines. Numerical simulations show that the lateral field strength that is generated at the edge of a metal line is the same order of magnitude as the perpendicular accelerating field strength (~10⁶ V/m) necessary for imaging. Therefore, electrons emitted near the edge can be displaced from the image collection volume and generate contrast. Several well-characterized samples have been used to test this contrast mechanism when imaging with and without oxide-covered metal structures. We will show images of the lateral width of the edge-contrast increasing as the bias voltage is increased from 0 to ± 10 V. The magnitude of the edge effect observed for a metal line buried under 4.5 nm of SiO₂ is comparable to an uncovered metal line. Numerical studies suggest that the bias voltage necessary to minimize the edgecontrast increases about 2.5 mV per nanometer increase in height. Thus, image analysis of this effect may allow for height determination of structures. Moreover, this contrast mechanism could also be used in failure analysis by helping to identify breaks in metal lines. *Supported by LPS and in part by the NSF-MRSEC. .

¹ V.W. Ballarotto, K. Siegrist, R.J. Phanuef and E.D. Williams, J. Appl. Phys. 91, 469 (2002).

² V.W. Ballarotto, K. Siegrist, R.J. Phanuef and E.D. Williams, Appl. Phys. Lett. 78, 3547 (2001).

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