# Monday Morning, November 4, 2002

## Applied Surface Science
## Room: C-106 - Session AS-MoM

## SIMS
## **Moderator:** F.A. Stevie, North Carolina State University

8:20am **AS-MoM1 Maximizing and Automating Information Extraction in Time-of-Flight Secondary Ion Mass Spectrometry**, ***S.J. Pachuta***, 3M Company

Numerical techniques have been found useful in extracting information from the large data sets produced by time-of-flight secondary ion mass spectrometry (TOF-SIMS). Simple univariate approaches to quantitation in static SIMS, including spectral normalization, smoothing, curve fitting, and generation of spectral overlays, will be described. The complexity of TOF-SIMS data makes multivariate approaches particularly useful, and multivariate statistical techniques such as principal components analysis (PCA) will be described in detail. PCA, in simplest terms, reduces a data set to its essential elements. A significant advantage of PCA over univariate methods is that it greatly compresses the data by combining variables. This is particularly beneficial in TOF-SIMS, where a data set may consist of a 256x256 pixel matrix in which each pixel contains a complete mass spectrum consisting of upwards of 100,000 mass channels. Applications of PCA which will be described here include automating complex tasks previously performed manually by the analyst, finding non-obvious information in data sets, and distinguishing relevant from non-relevant information. Situations in which PCA is particularly applicable are those in which differences are sought. Typical examples might be a comparison of spectra from a series of materials with different performance characteristics, or chemical imaging of a surface. Automation of some common imaging tasks, such as choosing which peaks to map or extracting spectra from regions of interest, is one of the key concepts to be presented.

8:40am **AS-MoM2 G-SIMS - Molecular Structure**, ***I.S. Gilmore***, *M.P. Seah*, National Physical Laboratory, UK

G-SIMS or gentle SIMS has already been demonstrated to provide a straightforward way to simplify static SIMS spectra.[1,2] These spectra are composed of parent fragment ions amongst a large number of high intensity degradation products. The fragmentation is quantified in terms of the partition functions of the fragments emitted from a surface plasma with effective temperature, $T_p$. It is found that fragmentation is least for high mass incident ions at low energies. By extrapolation of the data to low $T_p$, a new spectroscopy, known as gentle-SIMS or G-SIMS is formed. The significant peaks in the G-SIMS spectra are those peaks which would be emitted as a result of an ion impact that generates a surface plasma of very low $T_p$ and thus have little post-emission rearrangement or fragmentation. Those peaks are, thus, directly characteristic of the material without rearrangement and enable direct interpretation and identification. G-SIMS has been successfully tested on a range of polymers, molecules and complex organics.[3] G-SIMS not only provides the parent molecule mass, and hence composition in terms of numbers of C,H,O,N etc atoms, but is also allows the molecular structure to be evaluated. Current work explores the re-building of parent molecules using the fragmentation pathways which are mapped out as $T_p$ is varied. This new dimension to the technique has significant potential information not previously obtainable in static SIMS. G-SIMS-MS has some of the attributes of MS-MS. These effects and the use of G-SIMS with mixtures will be discussed.

[1] I S Gilmore and M P Seah, Appl. Surf. Sci. 161 (2000) 465.

[2] I S Gilmore and M P Seah, SIMS XIII proc, Appl. Surf. Sci. in the press.

[3] I S Gilmore and M P Seah, Appl. Surf. Sci. 187 (2002) 89.

9:00am **AS-MoM3 Recent Advances in Time-of-Flight SIMS**, ***E. Niehuis***, ION-TOF GmbH, Germany **INVITED**

When TOF-SIMS was introduced in the early 80's, it appeared to be the ideal instrument for surface analysis in static SIMS mode. It's most striking features were a very high transmission close to 100 %, a parallel detection of all masses and an unlimited mass range. At that time, the current density of the pulsed primary ion beam was so low that the lifetime of the uppermost monolayer exceeded thousands of seconds. Early applications of TOF-SIMS focused on the analysis of involatile molecules, prepared as thin layers on metal substrates. Improvements in mass resolution to a level above 10,000 and the development of an efficient charge compensation opened many new fields in surface analysis, like the detection of trace elements and surface analysis of bulk organic materials such as polymers. The combination with liquid metal ion guns towards the end of the 80's added powerful imaging capabilities with a lateral resolution well in the sub-micron range. In the mid 90's, TOF-SIMS started to become a depth profiling technique using the so-called dual beam mode. A low energy sputter gun was applied for sample erosion with a reasonable speed while the center of the sputter crater was analyzed with the pulsed high energy beam. In the recent years, TOF-SIMS has become a very powerful depth profiling technique with applications ranging from the analysis of ultra-shallow implants to the profiling of thick films. The combination of a small spot analytical beam with a low energy sputter beam offers new capabilities in 3-dimensional micro analysis. In this paper recent developments in TOF-SIMS instrumentation will be discussed and analytical examples from a variety of different fields will be given to highlight the capabilities of the technique.

9:40am **AS-MoM5 Applications of Time-of-Flight Secondary Ion Mass Spectrometry in Materials Research**, ***B.W. Schueler***, Physical Electronics **INVITED**

TOF-SIMS has gained increasing acceptance as a surface analysis techniques in scientific research and industrial applications. The most important features of the technique are its ability to (parallel) detect and identify all secondary ion species (molecular and organic)over a virtually unlimited mass range with high sensitivity. These properties result in an extremely efficient utilization of information from the analytical area and high detection sensitivity for identifying organic molecular species as well as trace element contaminants. The use of micro-focused primary ion beams enables measurement of the lateral surface distribution of molecules and atomic ion mapping with ~100nm resolution. Ion bombardment of organic surfaces results in the emission of characteristic fragments of the molecule and often the complete ionized molecule, providing a "fingerprint" spectrum of the molecule. This fingerprint may serve as unambiguous identification of the molecular species and functional groups. Parallel detection and high sensitivity of TOF-SIMS are equally important in inorganic (surface) analysis. For example, trace silicon surface metal contamination levels in the 0.1-1ppm levels across the periodic table are readily achieved. TOF-SIMS surface metal detection limits in Si are typically 10-100 times lower than those achievable by standard TXRF (Total Reflection X-Ray Fluorescence). This paper is intended to illustrate some key analytical and problem solving capabilities of TOF-SIMS with a range of materials research applications. The emphasis will be on semiconductor-related applications such as surface metal contamination transfer in process equipment, organic/inorganic contamination and etch/rinse residues, and depth profiling. Applications from the disk drive, and polymer industry will also be included. The relative merits of TOF-SIMS and other surface analysis techniques (i.e., XPS, AES, TXRF, etc.) will be discussed.

10:20am **AS-MoM7 Method to Quantify the Comparison of Predicted vs. Experimental Isotopic Clusters in Time of Flight Secondary Ion Mass Spectrometry for High Mass Peak Identification**, ***R.W. Nowak***, *C.M. Mahoney*, State University of New York at Buffalo, *A. Hawkridge*, University of Arizona at Tucson, *J.A. Gardella*, State University of New York at Buffalo

Investigation of the high mass range of the ToF-SIMS spectrum (800-4000 Da.) will yield information on long range polymer interactions which affect ion formation and will provide information about the long range forces between polymer chains. Peak assignment in the high mass region is not as straight forward as in the low mass region. Isotopes of the atoms that make up the fragments combine to yield clusters of peaks, not just single peaks as seen in the low mass regions. We are able to assemble predicted isotopic clusters to compare with the collected experimental data for identification. In past reports visual comparisons of the predicted and experimental isotope cluster results were used to judge the goodness of fit between two data sets. We have developed an analytical method to construct correlation plots for comparison with these data sets and to quantify the goodness of fit between the predicted and experimental results. This paper will illustrate a method to create correlation plots of the predicted vs. experimental results. Clusters from atomic constituents in the low mass region are used as a simple model to demonstrate the application. High Mass clusters from several previously published ToF-SIMS of high mass polymers will be utilized to show the effectiveness of this method.

10:40am **AS-MoM8 TOF-SIMS Characterization of Mixed Decanethiol - Octadecanethiol Self-Assembled Monolayers**, ***D.J. Graham***, *D.G. Castner*, University of Washington

Previous work in our labs has demonstrated the utility of TOF-SIMS in determining detailed chemical and structural information from self-assembled monolayers (SAMs). Much of this work has been done with homogeneous SAM surfaces. This study presents an investigation of a more complex mixed monolayer system using methyl-terminated SAMs. Other studies using mixed SAMs have used thiols with unique head groups to exploit a surface property or chemical signature. Thus, using methyl terminated SAMs increases the difficulty of interpretation due to the fact that there are no unique atoms to exploit between the thiol molecules. For this study, mixed monolayers of decanethiol (C10) and octadecanethiol (C18) were prepared from 1mM solutions at various mixture ratios (v/v). Using TOF-SIMS multivariate and univariate analysis, we demonstrate that the molecular specific information generated by TOF-SIMS enables both a detailed characterization of the mixed monolayer films and insight into their structure and surface arrangement. XPS analysis showed only the presence of the expected elements with all sulfur bound to the gold surface. Surface concentrations estimated by TOF-SIMS and XPS showed a significant enrichment of the longer chain thiol. Monitoring the yield of specific molecular ions in the TOF-SIMS spectra gave insight into the arrangement of the thiols on the gold surface. In particular the yield of the cluster ion Au[MC10-H][MC18-H] suggested the samples were phase segregated at least at a nanometer scale. Multivariate analysis of the TOF-SIMS data captured the changing composition across the series, and also highlighted structurally specific information about each thiol.

11:00am **AS-MoM9 Secondary Ion Emission from Thick Organic Films: Influence of Primary Ion Bombardment Conditions**, *E. Tallarek*, Tascon GmbH, Germany, *F. Kollmer*, ION-TOF GmbH, Germany, *B. Hagenhoff*, ***R. Kersting***, Tascon GmbH, Germany

Our ongoing studies focus on the secondary ion emission from thick organic layers under different primary ion bombardment conditions. As model analyte system spin coated layers of the polymer additve Irganox 1010 on low density polyethylene (LDPE) was used because the collision cascade takes place completely in organic material (simulation of "real" polymer conditions), the analyte of interest is only present in the uppermost monolayer (no contribution from deeper layers) and shows characteristic secondary ions covering the complete mass range from 1-1000u whereas the aliphatic substrate polymer LDPE emits ions only in the low mass range. The secondary ion parameters yield Y, disappearance cross-section $\sigma$ and secondary ion emission efficiency E (yield per damaged area) were determined for primary ion bombardment with several monoatomic as well as polyatomic primary ions including $Ga^+$, $Cs^+$, $Au^+$ as well as $SF_5^+$, $Au_2^+$ and $Au_3^+$. Additionally, the primary ion energies were varied between 4 and 25 keV. The results can be summarized as follows: For monoatomic primary ion bombardment the efficiency increases with the primary ion mass. Maximum enhancement factors compared to $Ga^+$ bombardment are about 5-10. Polyatomic primary ion bombardment leads to enhancement factors of at least 60. Optimum primary ion energies depend on the respective ion species. These results have consequences for the achievable lateral resolution in ion imaging as well as for the detection limits in surface spectrometry. Examples will be given.

11:20am **AS-MoM10 A New Approach to Measuring the TRUE Boron Profile Near the Si Surface using SIMS**, *T.H. Büyüklimanli*, ***J.W. Marino***, *C.W. Magee*, Evans East

To date, SIMS measurements of the B distribution in the near-surface region have been made using an oxidizing ambient formed by either O2 flooding or by using normal incidence O2 bombardment to avoid possible near surface artifacts. However, the shape of the B depth profile obtained under these conditions at or near the surface has always been questioned. Separate measurements by poly-Si-encapsulation SIMS, RBS, ERDA and TEM have shown an implant peak below the surface contrary to the peak at the surface as usually depicted by SIMS with oxidizing ambient. Our paper investigates whether or not the apparent problems of profiling ULE B in Si under fully oxidizing conditions can be obviated by sputtering with oxygen under conditions that are not fully oxidizing. Correct measurement of the B profile shape in the top 1-2 nm of the sample would be useful to the TCAD modeling community. Our tests show that the B+ relative sensitivity factors with respect to Si+ were identical for both Si and SiO2. This suggests that the matrix effect due to the presence of surface oxide can be avoided by simply point-by-point normalizing the B+ intensity to the interpolated Si+ intensity. However, proper characterization of the detector electronics is required to record intensities accurately. The profiles acquired using low energy O2 bombardment at 60° incidence and processed using interpolated normalization resulted in doses matching values measured by nuclear reaction analysis (NRA). The profiles also show that B implant peaks for the range of low energies measured are, indeed, below the surface as measured by ERDA, RBS, TEM and poly-encapsulation SIMS. Another benefit of depth profiling without full oxidation is the ability to detect the surface oxide and location of the B implant with respect to the oxide. Profiles acquired under oxidizing ambient require a separate measurement to determine the oxide thickness and to correct for sputter rate changes from the oxide into the Si.

11:40am **AS-MoM11 Study of Electron Beam Excited Plasma SNMS for High Detection Sensitivity**, ***T. Noguchi***, The Graduate University for Advanced Studies, Japan, *S. Kato*, KEK & The Graduate University for Advanced Studies, Japan

SNMS has been developed for years to obtain precise depth profiling and high quantificability conquering the problems of SIMS. SNMS based on electron beam excited plasma (so called SNART: Sputtered Neutral Analysis-Riken Type) has several advantages; the high detection sensitivity with a high post ionization efficiency, the high depth resolution with low energy sputtering less than 100eV keeping a high sputtering rate, the relatively simple structure of the apparatus, the small dispersion of relative elemental sensitivity factors and the capability of insulator analysis without a charge neutralizer. In this study we attempted to improve the apparatus so as to obtain a higher sensitivity with maintaining a high depth resolution of around 1 nm. For this purpose, we have adopted a ToF mass spectrometer and made the plasma source be able to work in UHV. Detection sensitivities for metal surfaces were estimated to be less than 1 at.ppm keeping the high depth resolution on the basis of our preliminary experimental results of a sputtering rate, a post-ionization efficiency, a transmission of the ion optics and a total gain of the detection system. We will report our hardware development and results of experimental data compared with the estimated numbers.

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