Thursday Evening Poster Sessions, November 5, 1998

Applied Surface Science Division
Room Hall A - Session AS-ThP

Aspects of Applied Surface Science Poster Session

AS-ThP1 Mass Spectral Frequency Plots: A New Tool For Static SIMS Data Interpretation*, **A.M. Spool,*** IBM Corporation

The experienced Static SIMS Analyst will examine common peak mass differences in addition to common peak positions in attempting to interpret a spectrum of a new or unknown sample. Mass differences of 44 amu, for example, suggest polymers with an ethylene oxide monomer, common to many surfactants. Many species with biological origins will display peaks differing by 2 methylene groups (28 amu). Fluorinated polymers will often have peaks with mass differences of 50 amu corresponding to a perfluorinated methylene. Spectra of many polymers will have common peak differences that correspond to the mass of their monomers. In this paper I propose a simple algorithm that converts spectra with unit mass resolution to a plot of the "frequency" of peaks in the mass spectrum. The resulting "pseudo-power spectra" or "mass spectral frequency plots" are more indicative of the type of species on the sample than the exact identity of these species. The algorithm proposed simply involves multiplying the intensity of the peak at each mass by the peak intensity at every other mass, and adding each result to the bin corresponding to the difference between the masses. The intensities of the resulting peaks at each "delta" are a function of the number of peaks with those mass differences, and the intensities of the original peaks. Examples of these plots will be shown and their utility demonstrated.

AS-ThP2 The Münster High Mass Resolution Static SIMS Library*, **B.C. Schwede,*** University of Münster, Germany*; T. Heller, D. Rading, E. Niehuis,* ION-TOF GmbH, Germany*; B. Hagenhoff,* TASCON GmbH, Germany*; L. Wiedmann, A. Benninghoven,* University of Münster, Germany

Despite the high mass resolution and accurate mass determination available with high-performance TOF-SIMS instruments, the interpretation of a TOF-SIMS spectrum is a tedious process. This paper describes the "Münster High Mass Resolution Static SIMS Library" which can support the user in this situation. The reference spectra were collected with various state-of-the-art TOF-SIMS instruments at the University of Münster, at ION-TOF and at TASCON. The library contains positive and negative spectra from a large variety of substances, with special emphasis on polymers, additives and semiconductor materials. It is structured in a hierarchical, easily extendable manner. All reference spectra are included in the library as interpreted lists of peaks. This library is embedded in the TOF-SIMS IV software package which offers tools like a reference browser or a facility to list all reference spectra which include specified peaks. The evaluation tools are based on a search algorithm specifically designed for the identification of compounds in mixtures. In order to evaluate the similarity of spectra, a version of the PBM algorithm@footnote 1@ was adapted to the specific needs of TOF-SIMS. The performance of the search algorithm was tested by analyzing mixtures of two substances with known composition. The results will be presented and compared to those achieved using principal component analysis (PCA) and neural networks. @FootnoteText@ @footnote 1@ F.W. McLafferty, R.H. Hertel, R.D. Villwock, Organic Mass Spectrometry 1974, Vol. 9, pp. 690-702

AS-ThP3 Formation of Alkanethiol Self-Assembled Monolayers on Oxidized Gold Surfaces*, **C. Yan,** A. Gölzhäuser, M. Grunze,* Universität Heidelberg, Germany*; C. Wöll,* Ruhr-Universität-Bochum, Germany

The formation of alkanethiol self-assembled monolayers (SAM) on oxidized gold was studied by x-ray photoelectron (XPS), near edge x-ray absorption fine structure (NEXAFS) and infrared spectroscopy. Different oxidation procedures, exposure of gold to atomic oxygen in vacuum and to UV/ozone in air, lead to different types of surface gold oxides, distinguishable by their oxygen XP spectra. On the gold oxide formed by exposure to atomic oxygen stable SAMs were formed from ethanolic solution as well as via vapor deposition. Two sulfur species were distinguished by XPS, gold thiolate and a species related to the reaction of the thiol with the oxide that was found encapsulated under the self-assembled monolayer. The monolayers adsorbed from ethanolic solution were denser packed and less tilted than the layers formed by vapor deposition and SAMs on clean gold surfaces. The gold oxide produced by exposure to UV/ozone in air was removed during thiol adsorption from ethanolic solution and a monolayer assembled on the bare gold. Chemical vapor deposition on this oxide did not lead to well defined monolayers.

AS-ThP4 XPS and ISS Study of X-ray Damage of Alkanethiol Self-Assembled Monolayers on Gold and Silver*, **D.E. King**, L.S. Dake, A.W. Czanderna,* National Renewable Energy Laboratory

X-ray photoelectron spectroscopy (XPS) has been extensively used to study the chemistry of self-assembled monolayers (SAMs). While XPS is often considered the most non-destructive surface analysis technique, it is known that X-ray exposure and the resulting secondary electron emission can alter the reactivity of many materials. Organic materials can be particularly susceptible to damage resulting from X-ray bombardment during XPS. We have studied the effects of both Mg and Al K-alpha X-ray exposure on acid and methyl functionalized alkanethiol SAMs on gold and silver substrates. In the methyl terminated SAMs, a 20 percent reduction in C 1s peak area results after a 3 hour X-ray exposure. In the acid-terminated SAMs, both carbon and oxygen XPS signals decrease rapidly, with a relatively greater loss in the oxygen signal. Ion scattering spectroscopy (ISS) depth profiles indicate that it takes longer to sputter the irradiated SAMs than non-irradiated SAMs. We conclude that chemical changes in the monolayers result from the X-ray exposure. Although these changes are not detectable with XPS, the increased resistance to sputtering by the ISS beam indicates changes in bonding that are consistent with C-C crosslinking between the chains in the SAMs. XPS and ISS data will be presented for methyl and acid terminated alkanethiols after subjecting the SAMs to increasing times of X-ray exposure. This work was performed under DOE contract DE-AC36-83CH10093 @FootnoteText@ After Aug. 1, address for Dr. L. S. Dake is Susquehanna University, Selinsgrove, PA 17870-1001

AS-ThP5 Identification of Halogen Atoms in STM Images of Substituted Phenyloctadecylethers*, **H.S. Lee**, S. Iyengar, I.H. Musselman,* University of Texas, Dallas

A homologous series of para-substituted phenyloctadecylethers (X-POEs, X = H, Cl, Br and I) was prepared and characterized using @super 1@H NMR and GC/MS. Scanning tunneling microscopy (STM) images acquired from these ethers have revealed a bias-dependent contrast which corresponds to calculated electron density contours of various X-POE molecular orbitals. STM images of the X-POEs reflecting the electron density contour of the highest occupied molecular orbital (HOMO) exhibited four bright spots - one for the halogen atom, two representing the pair of lobes of the phenyl ring, and one for the oxygen/alpha-carbon atoms. For each X-POE, a minimum of three sets of four submolecular resolution HOMO images were acquired. The intensities of the spots for the halogen atom and the lobe of the phenyl ring closest to the halogen were measured and their ratio was calculated. The ratios for Cl-POE, Br-POE and I-POE were 0.48 ± 0.05, 0.58 ± 0.05 and 0.75 ± 0.07, respectively. An analysis of variance revealed that the intensity ratios of the X-POEs could be clearly distinguished among all data sets.@footnote 1@ @FootnoteText@ @footnote 1@ The support of this research by a grant from the Robert A. Welch Foundation is gratefully acknowledged.

AS-ThP6 Identification of Surface Nitrogen Functionalities Using Gas Phase Derivatization and XPS Analysis*, **Y. Liu,** L.J. Gerenser, P.M. Thompson, J.M. Grace,* Eastman Kodak Company

X-ray photoelectron spectroscopy (XPS) has been widely used as a primary surface analytical technique to determine the surface atomic compositions of polymeric materials. It provides quantitative elemental composition with excellent surface sensitivity. However, quite often, it is very difficult to identify the functional groups when the core-level binding energy shifts of these species are small. We have developed an approach using gas phase derivatization reactions in combination with XPS surface analysis for semi-quantitative determination of nitrogen functional groups. This poster will focus on the studies of two derivatization reagents, trifluoroacetic anhydride and trifluorotolualdehyde, and their applications in the identification of nitrogen functionalities including primary and secondary amines, amides and nitriles.

AS-ThP7 In-situ Characterization of Plasma Polymerized Films Using External Reflection Infrared Spectroscopy*, F.J. Boerio,* ***R.H. Turner,*** University of Cincinnati

External reflection infrared spectroscopy was used for the in-situ characterization of plasma polymerized films of acetylene, hexamethyldisilazane (HMDSZ), and hexamethyldisiloxane (HMDSO) as a function of thickness. The films were deposited onto polished iron and aluminum substrates in an inductively coupled RF reactor interfaced to an FTIR spectrometer. In-situ characterization of the films enabled the effects of oxidation during atmospheric exposure of the films to be reduced or eliminated. Conducting the investigations as a function of film thickness enabled spectral features associated with the bulk of the films and with the film/substrate interface to be identified. Infrared spectra of plasma polymerized acetylene films on iron substrates were characterized by a band near 3325 cm@super -1@ that was tentatively assigned to CH stretching in an acetylide species at the interface and by a band near 3300 cm@super -1@ that was assigned to the CH stretching vibration in mono-substituted acetylene groups in the bulk of the films. In a few cases, infrared spectroscopy was used to investigate adsorption of the neat monomers onto the substrates. Thus, infrared spectra of HMDSZ monomer adsorbed onto iron substrates were characterized by bands assigned to siloxane bonds, indicating some polymerization of the monomer.

AS-ThP8 X-Ray Microanalysis Inverse Modeling@footnote 1@, ***H.W. Wagner***, *W.S.M. Werner, H. Störi,* Technische Universität Wien, Austria

The typical electron interaction volume in electron microprobe analysis (EPMA) is in the order of several cubic microns. For a single spot measurement of a sample with complex geometry, the source distribution of characteristic x-ray signals within this volume cannot be determined, therefore making it impossible to gain information on the sample structure. A set of measurements performed under different conditions (e.g. beam energies, incidence angles) does contain structural information, however not in a readily available form. The present work describes an approach for the extraction of structural information from EPMA measurements. The inverse modeling method relies on an efficient way to compute the forward transformation, i.e. the calculation of a generated x-ray signal of a known structure and experimental setup, and the application of appropriate mathematical optimization techniques. The use of simulated annealing as optimization method turned out to be advantageous in this context. The presented approach can be applied to arbitrary 2-D structures and accounts for possible a priori information on the sample structure. @FootnoteText@ @footnote 1@ The authors wish to thank Digital Equipment Corp. for support of this work.

AS-ThP9 Analysis of X-ray Growth Oscillations During Heteroepitaxy, ***J. Baker***, Risoe National Laboratory, Japan; *F. Berg Rasmussen, M. Nielsen, R. Feidenhans'l,* Risoe National Laboratory, Denmark

Despite recent progress,@footnote 1@ x-ray intensity oscillations recorded during heteroepitaxial growth are an under-exploited source of information on buried interface roughness, growth-front roughness, and inter-layer spacings. We explore some fundamental aspects of growth curve shape and their dependence on the x-ray scattering vector and film properties. In particular, the super-periodic modulation of oscillation amplitudes is demonstrated. Oscillations during the growth KCl/NaCl(001) are shown as a typical example of the phenomenon. @FootnoteText@ @footnote 1@E. Weschke, C. Schüssler-Langeheine, R. Meier, and G. Kaindl, Phys. Rev. Lett. 79, 3954 (1997).

AS-ThP10 Surface X-ray Diffractometer for MOVPE growth at SPring-8, ***T. Kawamura***, *Y. Utsumi, M. Sugiyama, Y. Watanabe,* NTT Basic Research Laboratories, Japan; *J. Matsui, Y. Kagoshima, Y. Tsusaka,* Himeji Institute of Technology, Japan

We developed a grazing incidence x-ray diffractometer, installed at the SPring-8 synchrotron facility, to enable the analysis of the initial stage of III-V compound semiconductor homoepitaxial growth in gas-phase. To maintain growth conditions, the z-axis arrangement is used instead of the conventional 4-axes arrangement. The detection range of x-rays is from -5.0 degrees to 135 degrees in 2@theta@, and the incident and the take-off angle ranges from 0 degrees to 15 degrees. To align the goniometer system, additional stages were attached for horizontal and vertical translation, and rotation around the z-axis. The material gases are delivered with a conventional MOVPE gas handling system, consisting of carrier gas supply, material gas handling, and exhaust subsystems. Hydrogen and nitrogen are used for carrier gases, and organometallic vapor sources are selected for material gases. For safety, to avoid the leaks, the whole system, including the goniometer, were installed in an isolated and the cabinet is maintained at lower than atmospheric prresure.

AS-ThP11 Quantitative Wafer Surface Trace Metal Analysis by TXRF and Surface SIMS, *J.M. Metz, S.P. Smith,* ***M.J. Edgell***, *V.K.F. Chia,* Charles Evans & Associates

Ultra-clean Si wafer surfaces are critical to the fabrication of ULSI devices. This is reflected by the stringent contamination limits for polished and epitaxial substrates, and surface preparation (i.e. before gate oxide growth) suggested by the National Technology Roadmap for Semiconductors (NTRS). Today's requirement for surface metals is typically in the range of 10@super 10@ atoms/cm@super 2@. Future needs in the year 2003 are anticipated to be 1x10@super 10@ atoms/cm@super 2@ for Al, Ca, and Zn, and 2x10@super 10@ atoms/cm@super 2@ for Fe, Ni, Cu, and Na. The transition metals Fe, Ni, Cu, and Na are considered to be very damaging at the gate oxide level, and therefore requirements for these are becoming more stringent. It is even considered that surface metals on epi substrates before gate oxidation may have to be as tight as for polished substrates, because the low temperature processing at small design rules leads to less effective gettering in the p+ substrate of p/p+ epi. Al is important to monitor because at concentrations below 10@super 11@ atoms/cm@super 2@ it can increase the oxide growth rate in the very thin gate oxide regime. This is a different effect compared to higher levels of Al (e.g. >10@super 12@ atoms/cm@super 2@) decreasing gate oxide thickness for thicker gate oxides. TXRF and SurfaceSIMS are two of the most powerful analytical techniques available for substrate and interface engineering. Both these techniques provide quantitative trace metal information at the surface of wafers. TXRF is an excellent survey tool capable of analyzing 300 mm wafers to a depth of about 50 Å. Quantification at the Si/SiO@sub 2@ interface is very important and may be performed accurately using SurfaceSIMS. The information provided by these two techniques allows pre-clean technologies used on silicon substrates to be evaluated. This presentation reviews the two techniques and illustrates with examples how they compliment each other.

AS-ThP12 AFM Explanation of the Improved Resolution in Auger Depth Profiles by Using the Zalar Rotation, ***L. Lozzi***, *S. Santucci, D. Pacifico, P. Picozzi,* Università dell'Aquila, Italy; *R. Alfonsetti,* Texas Instruments ITALIA, Italy

Auger Microscopy, as a consequence of its high lateral resolution (around 10 nm) and its sensitivity to the surface, is a powerful tool to investigate elemental and chemical composition of surfaces, interfaces and thin films, particularly in microelectronics artifacts with dimensions lower than 200 nm. In this paper we studied the TiN/AlSiCu interface, with interfacial oxygen, of a 500 nm wide metal line of a 64 Mbit DRAM device. The sharpness of this interface and the presence of interdiffused interfacial contaminants may affect the device behaviour. The elemental depth profile of the investigated system has been performed by using the Auger Spectroscopy assisted by Ar ion sputtering. The profiles have been performed using two different methods of sample sputtering: the first one maintaining the sample in a fixed position respect to the ion beam and the second one by rotating the sample with a Zalar rotation accessory. The profiles have been interrupted when the TiN/AlSiCu interface had slightly overcome. The sputtering crater has been observed by using an AFM microscope. For identical samples we observed, in the case of the fixed sputtered sample, a particularly rough TiN/AlSiCu interface with evident finger prints of preferential sputtering which produces a sensibly enlarged interface depth profile. In the case of the rotated sample, we obtained a sharp interface profile which corresponds to a flat surface of the bottom of the crater with a roughness comparable to that of the not sputtered surface. In this case the presence of interfacial oxygen bonded to Al has been carefully localised.

AS-ThP13 Structure of Plasma Polymerized SiO@sub2@Films: Corrosion Protection of Steel and Aluminum Substrates, ***R.G. Dillingham***, Brighton Technologies Group, Inc.; *F.J. Boerio,* University of Cincinnati

Plasma polymerized organosiloxanes made using excess oxygen as a carrier gas have a silica-like structure, and function as excellent corrosion inhibiting coatings and primers for adhesive bonding and painting. Similar structures can be obtained using a variety of reactor configurations and polymerization conditions, but details of film structure and performance can vary. Infrared spectra of these films show non-bridging Si-O and -OH species. The relative amount of structural imperfection is a strong function of deposition conditions. These structural features provide reactivity necessary for adhesion of paints and adhesives, but limit corrosion protection, probably by increasing electrolyte diffusion. Structures that provide optimum corrosion protection do not necessarily provide optimum overlayer adhesion. This work relates film deposition conditions to structural defects, and shows how these defects affect the electrical impedance spectra and corrosion inhibiting capabilities of plasma polymerized SiO@sub2@.

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