Friday Morning, October 29, 1999

Applied Surface Science Division

Room 6A - Session AS-FrM

New or Improved Surface Related Analytical Techniques Moderator: P.M.A. Sherwood, Kansas State University

8:20am AS-FrM1 LEIS Measurement of Target Mass in the Presence of Inelastic Energy Losses@footnote 1@, *R. Bastasz, J.A. Whaley,* Sandia National Laboratories

Low-energy ion scattering (LEIS) is often used to identify the elements present on a surface. Peaks observed in the energy spectrum of scattered ions can be assigned to specific target masses. However, the usual kinematic expression that relates the energy of a scattered projectile to a target atom mass does not account for inelastic losses, such as ion neutralization/reionization and excited state formation, which can significantly affect the scattered-ion energy. We have developed a simple method for unambiguously determining target atom mass from LEIS measurements regardless of the amount of inelasticity in the collision. Analysis of the scattering kinematics with an included inelastic loss term shows that the scattered particle velocities form a circle in the polar coordinate system (v@sub n@,@theta@), where v@sub n@ is the normalized scattered-ion final velocity and @theta@ is the laboratory scattering angle. While the circle radius changes with the degree of inelasticity, the circle center depends only on the target-to-projectile mass ratio. So, by measuring ion energy spectra at three or more scattering angles, it is possible to construct the appropriate scattering circle, find its center, and deduce the target mass. The only assumption in the method is that inelastic losses are not a function of the impact parameter. This assumption appears reasonable at typical observation angles, as can be illustrated with several examples of inert-gas scattering from low-Z metal surfaces. @FootnoteText@ @footnote 1@ This work was supported by the US Department of Energy under contract DE-AC04-94AL85000.

8:40am AS-FrM2 Atmospheric Electron X-ray Spectrometer, J. Feldman, J.Z. Wilcox, T. George, Jet Propulsion Laboratory; D.N. Barsic, A. Scherer, T. Doll, Caltech

Atmospheric Electron X-Ray Spectrometer (AEXS) J. Feldman, J. Z. Wilcox, and T. George, Jet Propulsion Laboratory D. N. Barsic, T. Doll, and A. Scherer, Electrical Engineering and Applied Physics, Caltech Abstract The Atmospheric Electron X-ray Spectrometer (AEXS) is a new miniature instrument being developed for in situ elemental analysis of surfaces. The key component of the instrument is a microfabricated silicon nitride membrane. This electron transmissive membrane serves to isolate the high-vacuum electron column from the ambient atmosphere. An electron beam generated and focused in the column is transmitted through the membrane to impinge on the sample in the ambient atmosphere. The electron beam excites characteristic x-rays, which are analyzed to determine the elemental composition of the irradiated portion of the sample. The power of this type of analysis is that samples can be analyzed in situ without being introduced into a vacuum chamber as in traditional scanning electron microscopy (SEM). Due to the return ionization path through the atmosphere, sample preparation is unnecessary even for nonconductive samples. This talk describes the development and current status of the AEXS. Initial spectra were obtained in ambient Earth atmosphere with a spot size of less than 1mm and a spectrum acquisition time of a few minutes. The physical properties of a number of candidate low atomic number microfabricated membranes, including electron and xray transmissivity, will be discussed. The prototype instrument is designed to be portable, with a mass of 1 kg. The high spatial resolution of the AEXS (as compared to alpha particle or x-ray fluorescence instruments) will enable mapping of compositional heterogeneities at a grain size level. In addition to applications in planetary exploration, the AEXS also has potential applications in industrial process monitoring and quality control.

9:00am AS-FrM3 Advances in X-ray Photoemission Spectroscopy at Very High Spatial and Spectral Resolution, *B.P. Tonner*, *R. Kneedler*, University of Central Florida; *K. Pecher*, California Institute of Technology; *T. Warwick*, Lawrence Berkeley National Laboratory INVITED

Soft x-ray undulator synchrotron radiation has resulted in dramatic improvements in the performance of x-ray photoemission spectroscopy (XPS)for the study of surfaces and shallow interfaces. The two main areas of improvement are in spatial resolution and spectral resolution, which, in combination, result in improved sensitivity of the technique. Recent work with complex surfaces, such as the surfaces of natural minerals, will be used to show that fundamental issues regarding surface composition of such materials can be resolved using XPS imaging and spectroscopy from

sub-micron areas. XPS microscopy is used to qualify surfaces for further analysis using high resolution photoelectron diffraction (XPD). XPD studies of large unit cell surfaces, and of mineral surfaces, will be selected to illustrate the precision of atomic geometry that can be determined. Examples will be drawn primarily from our work on copper sulfide, bixbyite, galena, and pyrite surfaces.

9:40am AS-FrM5 An Evaluation of the ALS Micro-ESCA Beam Line Performance for Small Particle Analysis, C.R. Brundle, Y. Uritsky, G. Conti, Applied Materials, Inc.; P. Kinney, MicroTherm, LLC; Y. Ynzunza, Intel Corporation; E. Principe, Charles Evans and Associates

Intel, Applied Materials, and the ALS synchrotron staff have developed a micro-ESCA beam line at the Advanced Light Source, LBL. One of the major objectives was to produce "user-friendly" analysis at a spatial resolution significantly beyond that available in commercial instrumentation. We review the status of the project using both test structures and real particle situations and conclude the following: 1) Usable signal intensities are attainable down to ~2 µm size features, the nominal X-Ray beam size. This is 5 to 10x better than the PHI Quantum 2000. 2) The sample handling and navigation system to find small features works well (considerably better than any commercially available approach on ESCA systems). 3) The availability of the NEXAFS operation mode, in addition to the ESCA mode, provides valuable additional chemical state delineation capabilities. 4) Charging issues for insulating films and particles need to be resolved. 5) Since the "turn-around" analytical time and spatial resolution will always be far worse than for commercial SAM, the practical usefulness of the beam line depends strongly on its enhanced capability, compared to SAM, for chemical state delineation using the ESCA chemical shifts and near-edge structure, and on the reduced beam effects compared to e-beam SAM.

10:00am AS-FrM6 A Study of TOF-SIMS for the Analysis of Metal Contamination on Silicon Wafers, *I.A. Mowat*, *T.J. Schuerlein*, *J. Metz*, *R. Brigham*, *D. Huffaker*, Charles Evans & Associates

The current methods of choice for the analysis of metal contaminants on silicon wafers are Total Reflection X-Ray Fluorescence (TXRF) and SurfaceSIMS. TXRF is a survey technique, with good detection limits for transition metals (e.g. down to 10@super 9@atoms/cm@super 2@ for some elements). SurfaceSIMS is not usually used as a survey technique, but it has high sensitivity for species such aluminum and alkali metals (species not detected well by TXRF). Time-of-flight SIMS (TOF-SIMS) is a technique which offers a surface survey of all metal contaminants, with good detection limits. This paper details the investigation of TOF-SIMS as a possible tool for such analyses. Under the high beam current conditions used, elemental information is obtained with high sensitivity (under certain conditions, the detection limit for iron can be below 10@super 9@atoms/cm@super 2@, and is much lower for the alkali metals). Experiments were carried out to investigate the accuracy and precision of TOF-SIMS analyses of Si wafers. The areas of interest were: (1) short term variability of data from a standard spin coated wafer; (2) long term variability (over approximately six months) of data from the same wafer; (3) investigation of factors affecting the detection limits achievable by TOF-SIMS; (4) cross correlation of TOF-SIMS with established techniques such as TXRF and SurfaceSIMS. Short term variability was determined to be in the range 10-12%, and long term variability was ~20%. Work is underway to investigate the sources of this variability. Detection limits were studied by assessing wafers from different sources in the semiconductor industry, and were found to vary by up to a factor of five. Cross correlation with both TXRF and SurfaceSIMS have proven to be a good source of information to increase the accuracy of TOF-SIMS measurements. The information obtained will help assess the suitability of TOF-SIMS as an additional method for metal contamination measurement on silicon wafers.

10:20am AS-FrM7 Fundamental Studies of Polymer and Protein Cationization by ToF-SIMS, *R Michel*, *R. Luginbuehl*, *D.J. Graham*, *B.D. Ratner*, University of Washington

Cationization of polymers, proteins and polypeptides is carried out on novel substrates with Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS). The surfaces consist of carboxylic terminated self-assembled monolayers with various metal ions such as Ag, Na, Li, TI, and Cu substituting the terminal hydrogen. The resulting surfaces are used as carrier substrates for deposition and analysis of polymers, proteins and polypeptides. Low (1 kD) and high (400 kD) molecular weight polyethyleneoxide (PEO) was deposited via spincoating while the proteins were adsorbed to the substrates. Previously published results show that cationization of polymers was achieved with the various selected metal ions from the carboxylic terminated groups. Complementary experiments

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carried out on non-substituted and methyl terminated self-assembled monolayers suggested that metal ions which are desorbed from the gold surface and therefore not in close proximity to the polymer do not cationize polymers and their fragments. The intensity of the cationized fragments were observed to be dependent on the metal ion used. Both cationized fragments and whole molecular species were observed for the 1kD PEO while on 400 kD PEO chain fragments of up n = 25 monomer units were detected. For protein samples using our substrate, detection of whole low molecular weight proteins up to 2 kD could be achieved with additional peak patterns indicating a loss of peptide- and sidechains.

10:40am AS-FrM8 Synchrotron TXRF Quantification Using Ion Implanted Standards, R.L. Opila, J.P. Chang, J. Eng, Jr., J.R. Rosamilia, Bell Labs, Lucent Technologies; P. Pianetta, Stanford University; F.A. Stevie, R.F. Roberts, M.A. Decker, Bell Labs, Lucent Technologies

Much of the difficulty in quantification using TXRF has been associated with problems in obtaining suitable standards. The quantification can be very accurate, but the standards to date are difficult to prepare and are not generally available. Ion implantation is often used for quantification of secondary ion mass spectrometry and can be obtained for any element, but the implanted distribution is not well defined at the surface. The technique of implantation through a sacrificial oxide layer has been applied to create TXRF quantification standards. Ion implants of Ca, Fe, Cu, Ni, As, and Sb were made through 0.1 µmm SiO@sub 2@ on Si substrates. Measurements were made using conventional and synchrotron TXRF after removal of the oxide. The results show that there is a direct correlation between the ion dose and the TXRF measured dose in the sampling depth for TXRF. Measurements were made using surface and time-of-flight SIMS, with similar conclusions. Certain elements, e.g., copper, are known to plate on the surface after oxide etch. One unique advantage of performing TXRF at the synchrotron is the ability to easily change the energy of the exciting x-rays. Using the dependence upon incident photon energy it is possible to collect a near edge absorption spectrum of the metallic species. This near edge spectrum then permits determination of the chemical bonding of the metallic element. By varying the angle of the incident x-rays above and below the critical angle, the difference in states between an impurity at the surface versus an impurity in the bulk can be determined. If metal remains on the surface, as suggested by the copper data, the surface copper can be removed. This removal was verified using synchrotron TXRF, XPS, and TOF-SIMS.

11:00am AS-FrM9 A Comparative Evaluation of FIB CVD Processes, B.I. Prenitzer, B.W. Kempshall, L.A. Giannuzzi, University of Central Florida; S.X. Da, FEI Company; F.A. Stevie, Cirent Semiconductor (Lucent Technologies) The metal chemical vapor deposition (CVD) capability available in focused ion beam (FIB) instruments has found multiple applications, e.g., in semiconductor device modification, for mask repair, and as a means to protect the region of interest during specimen preparation for electron microscopy. Added versatility has been afforded to CVD processes by the introduction of the dual beam FIBs. Dual beam instruments incorporate both an electron column and an ion column into a single FIB, and therefore allow the CVD process to be either ion or electron assisted. Evidence indicates that the mode of deposition may be significant in determining the final properties of the metal line, i.e., chemical composition and resistivity. In addition to the characteristics of the metal line itself, damage has been observed in the surface layers of specimens in which ion beam assisted CVD processes have been employed. Maintaining the integrity of the surface layers is particularly critical when preparing specimens for subsequent microstructural and/or microanalytical evaluation of ultrashallow regions. Cross-section transmission electron microscopy (TEM) is used to evaluate the surface integrity of single crystal Si substrates on which Pt metal lines have been grown by ion and electron beam assisted CVD processes. The effectiveness of various surface coatings in the prevention of radiation damage during ion beam induced CVD is also investigated.

11:20am AS-FrM10 High Resolution Sum Frequency Generation of a Rubbed Octadecyltriethoxysilane Self Assembled Monolayer on Glass, *T.E. Furtak*, *B.C. Chow*, Colorado School of Mines

Over the last decade, optical sum-frequency generation(SFG) has made the acquisition of vibrational spectra of surface species possible. However, the SFG instrumentation that has usually been employed suffers from low spectral resolution due to the use of band-width-limited picosecond lasers. Using a nanosecond source, we have been able to achieve a resolution nearly two orders of magnitude better than that characterized by a picosecond source. Exploiting this advantage we have observed previously

unresolved features in the vibrational spectra of rubbed self-assembled monolayers of octadecyltriethoxysilane(OTE) on glass. We have been able to establish a relationship between the effect which rubbing produces and the surface coverage of the molecule through the ratio of the chain - CH@sub 2@- and terminal -CH@sub 3@ features in the spectrum. This new insight will be of value to surface modification technologies, particularly those involving liquid crystal displays.

11:40am AS-FrM11 The Use of Field Ionization Methods to Probe the Influence of High Interfacial Electric Fields on Electrochemical Phenomena, V.K. Medvedev, University of Washington; D.L. Scovell, University of Washington, U.S.A; C.J. Rothfuss, E.M. Stuve, University of Washington

One characteristic of the electrode/electrolyte interface is the presence of high electric fields, typically on the order of 1 V/Å. With sharp field emitter tips, sufficiently high electric fields can be generated at the tip surface by application of a few kV bias potential. We have developed a field ionization microscopy and mass spectroscopy system for studying the influence of high electric fields on ionization of water. Water is adsorbed on a platinum field emitter • adjus 350 Å under both field-free and applied field conditions. Water adlayers ranging in thickness from 0 to 5000 Å have been examined at temperatures ranging from 30-300 K at pressures below 10@super -6@ torr. Water ionization was detected by time-of-flight and Wien filter (ExB) mass spectroscopies and imaged on a phosphor screen. Experimental and numerical results to date show that: (1) fields of only 0.2-0.5 V/Å can increase the ionic content of the water layer by several orders of magnitude; (2) the ions formed are hydrated by as many as 10 water molecules; (3) the onset of water ionization on a clean Pt tip increases linearly with temperature over the range of 170-300 K; and (4) ions formed at the tip/water interface must diffuse through the water layer prior to detection. The distribution (n) of (H@sub 2@O)@sub n@H@super +@ clusters is a strong function of ionization conditions and provides information on the nature of surface diffusion as a function of temperature. The diffusional barrier for ion transport through the water layer appears to be a function of applied electric field and the nature (amorphous vs. crystalline) of the water layer.

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