Tuesday Afternoon, October 3, 2000

Material Characterization Room 207 - Session MC-TuA

Quantitative Surface Analysis

Moderator: S. Hofmann, Max-Planck-Institute for Metals Research

2:00pm MC-TuA1 Molecular Secondary Particle Emission from UHV-Prepared Molecular Overlayers, A. Schnieders, M. Schröder, K. Rüschenschmidt, A. Benninghoven, H.F. Arlinghaus, Physikalisches Institut der Universität Münster, Germany

Secondary particle yields in organic SIMS and SNMS are not determined by the surface concentration of the respective particles only. Furthermore, the chemical interaction between substrate and adsorbed molecules determines the secondary particle emission, in particular from the first molecular monolayer. Especially the intrinsic ionization but also the fragmentation of the sputtered particles is influenced by this so-called matrix effect. Additionally, secondary particle emission depends on primary ion properties such as species or energy. In continuation of recent investigations, mainly focussing on the sputter process, we used UHVprepared molecular overlayers of adenine and alanine prepared on liquidnitrogen cooled substrates. We extended our investigations to a broader range of substrate/molecule combinations to determine the influence of the matrix effect. The flux of sputtered secondary neutrals and secondary ions in dependence on the layer thickness was continuously monitored under static sputtering conditions during overlayer formation. The detection of the sputtered neutrals was achieved by efficient laser postionization. As substrates we chose Au, Ag, Cu, Ni, Si, Al and C surfaces to cover different types of surface chemistry. A comparison between secondary ion and secondary neutral emissions showed a distinct ionization matrix effect depending on the respective substrate material for @beta@-alanine but not for adenine.

2:20pm MC-TuA2 Detection of Trace Metal Contamination on Si Wafers by TOF-SIMS, R. Möllers, T. Grehl, E. Niehuis, ION-TOF GmbH, Germany

According to the ITRS roadmap, the detection of metal trace impurities on wafer surfaces is becoming increasingly important. Analytical techniques with detection limits for transition metals and alkali metals well below 5E8 atoms/cm@super 2@ are required in the coming years. At present, TXRF is widely used for the detection of transition metals on blank wafers but it seems that its detection limits will no longer be sufficient in the future. The VPD based methods collect the contamination from the oxide of the entire wafer and techniques like VPD-AAS and VPD-ICMS can achieve detection limits in the low E8 range. However, they can not give information on the lateral distribution and do not discriminate against particle contamination. Time-of-Flight SIMS is an attractive candidate for the detection of trace metals. The analysed area is only about 50 to 100 μ m in size and the analysis for all elements in parallel takes only a few minutes per position on a wafer. Detection limits in the low E8 range can be achieved for a number of important metals. In combination with a stage raster, mapping of contaminants on large areas is possible. In contrast to the established techniques, TOF-SIMS can be applied to patterned wafers and the wafer back-side as well. On the other hand, the quantification in TOF-SIMS surface analysis has been a concern due to the well known matrix effect of SIMS and the rather small sampling depth of only 1-2 monolayers. In this contribution, we will discuss the capabilities of TOF-SIMS for trace metal analysis in more detail. We will focus on analytical protocols that give quantitative results and minimise the influence of the initial chemical state of the surface (organic contamination level, oxidation state etc.). The results will be compared to the established analytical techniques.

2:40pm MC-TuA3 Comparative Ion Yields by Secondary Ion Mass Spectrometry from Microelectronic Films, *C. Parks*, IBM Corporation

Secondary Ion Mass Spectrometry (SIMS) is reported from multipleelement ion implants. The implants include a thirteen element metal set dubbed the Universal Metal Standard (UMS) and a six element gas set called the Universal Gas Standard (UGS). These implants were made into films of interest for microelectronics (silicon, silicides, wiring layers, liner metals, organic dielectrics, and polymer dielectrics.) Because species are co-implanted, the relative sensitivity factor (RSF) for many elements are generated with each SIMS profile. Because the implant sets are selfconsistent, ion yields can be readily compared from matrix to matrix. The literature has compared ion yields within single matrices using the RSF. This study performs a broader comparison across matrices and requires a more general metric. In SIMS, the useful ion yields of potassium positive ions and chlorine negative ions approach a yield-saturating limit. To compare matrices, we obtain normalized useful yields (NUY), where the normalization is to the potassium or chlorine yields from silicon. In this paper we document the ion implants sets themselves, we show some of the SIMS profiles, and we note trends in ion yields and implications for SIMS analysis.

3:00pm MC-TuA4 Quantitative Surface Analysis Using Ion Implantation, F.A. Stevie, J.M. McKinley, C.N. Granger, Lucent Technologies; F. Hillion, CAMECA Instruments; D.S. Simons, P. Chi, National Institute of Standards and Technology; B. Schueler, Physical Electronics; C.B. Vartuli, T.L. Shofner, Lucent Technologies; L.A. Giannuzzi, University of Central Florida INVITED This paper summarizes current uses of ion implantation to quantify analytical data. SIMS is emphasized, but the methods are applicable to other techniques. SIMS requires secondary standards for calibration. Ion implantation has been traditionally used to create SIMS standards because any element can be implanted and the dose and energy tailored for the application. High reproducibility has been demonstated for SIMS measurements using these standards. Absolute dose measurements can be made for boron and arsenic using NIST reference materials. Quantification at a surface can be achieved using implantation through a removable layer by selecting the implant energy so that the peak of the implant is at the interface between the removable layer and the substrate. This mehod has been successful for surface SIMS, time-of-flight SIMS, and TXRF measurements. The dose can be increased to provide detection and quantification by other analytical methods, such as AES, XPS, and EDS. High dose quantification can also be used to quantify SIMS in the concentation range of a few percent. This is especially of interest for semiconductor materials, such as PSG, BPSG, and FSG, that are difficult to profile by other methods. SIMS line scan measurements can be quantified by first scanning over a series of depth profiles made at increasing depth into an ion implanted reference. Focused ion beam (FIB) workstations can be used to prepare cross sections of ion implanted standards that can be lifted out and mounted perpendicular to the analysis beam. Secondary ion images of the cross sections provide quantification of the element of interest. FIB prepared cross sections of high dose implanted standards can be used for AES and EDS calibration asnd for determination of detection limit.

3:40pm MC-TuA6 Comparison of ISS, XPS, and QUASES-XPS Techniques for Determination of Growth Mechanisms: Application to Thin Iron Oxide Films Deposited on SiO2, F. Yubero, A.R. Gonzalez-Elipe, Inst. for Material Science of Sevilla; S. Tougaard, University of Southern Denmark, Denmark We have studied the formation of iron oxides on SiO2 under varying growth conditions by X-ray photoemission spectroscopy (XPS) and ion scattering spectroscopy (ISS). Three different procedures for quantitative analysis of the experimental data were used: 1) traditional analysis of the XPS-peak intensity by assuming a layer formation that covers the surface completely, 2) combination of the XPS-peak and ISS intensities assuming a Poisson distribution of island heights, and 3) Tougaard-method (QUASES@footnote 1@) to determine in-depth profiles from analysis of the peak and background. The difference between the three methods lies mainly in the a priori assumptions made on the surface morphology. In contrast to method 1) and 2), the Tougaard-method is free from assumptions about the growth structure of the overlayer. By a critical comparison of the results, it is concluded that the Tougaard-method gives the most complete and reliable information. It is found that iron oxides on SiO2 grow with strong island formation, whose height depends on the preparation conditions of the deposit. The growth mechanisms are proposed. Thus, for example, if iron oxide is deposited on SiO2 at room temperature in a PO2 of 2Â'10-6 mbar, islands of ~22@Ao@ homogeneous thickness are formed for surface coverages below 20%. If the samples are annealed at 773K in a PO2 ~4Â'10-5, higher islands are formed (~32 @Ao@). For iron oxide treated by a plasma of oxygen, ~40 @Ao@ tall islands are formed for surface coverages below 30%. Besides, even ~35 @Ao@ of iron oxide does not fully cover the SiO2 substrate surface. Strong shadowing effects are observed in the ISS signal from the iron oxide deposits on SiO2 due to the tall island formation. As expected, the shadowing effects are stronger when taller islands have been formed. @FootnoteText@ @footnote 1@ http://www.quases.com

4:00pm MC-TuA7 Quantitative Depth Profiling with Angle Resolved XPS: The Effect of Surface Roughness, *S.M. Hunt*, Montana State University; *B.J. Tyler*, University of Utah

A major limitation of conventional XPS is that sample concentrations are calculated based on the assumption that the elemental concentrations are homogeneous in the outer 100 angstroms, an assumption that is frequently

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inaccurate. By exploiting the angular dependence of the XPS sampling depth, it is easy to get a qualitative assessment of surface uniformity, however, quantitative use of the data can be problematic. The objective of this work has been to explore the limits to which ARXPS data can be used for quantitative analysis of depth profiles and in particular to explore the influence of surface roughness on quantitation. Because calculating concentration depth profiles for ARXPS data is a mathematically unstable problem, modeling studies are necessary to determine how various sources of error propagate through the calculations. Assessing the influence of different types of error is of importance because even relatively small errors in the data might propagate into large errors in the calculated profiles. The influences of random error and surface roughness have been investigated. Monte Carlo simulations were used to explore the effects of random error. To explore the influence of roughness, simulations were used to calculate the XPS signal intensities from surfaces described by a 2 dimensional wave function. Various amplitude to wavelength ratios were explored. The influence on both the measure signal intensities and the calculated depth profiles has been investigated. The results have been validated on a series of samples consisting of self-assembled monolayers. Except at glancing angles, surface roughness has a minimal effect. At angles greater than 70 degrees from the surface normal, even minimal surface roughness can result in changes in the measured signal intensity of greater than 1000%. Optimum parameters for ARXPS experiments and the calculations have been identified.

4:20pm MC-TuA8 Intercomparison of IMFPs Determined by Elastic Peak Electron Spectroscopy, S. Tougaard, University of Southern Denmark, Denmark; M. Krawczyk, A. Jablonski, Polish Academy of Sciences; J. Pavluch, Dept. Electronics and Vacuum Physics, Czech Rep.; J. Toth, D. Varga, G. Gergerly, M. Menyhard, A. Sulyok, Hungarian Academy of Sciences

We have evaluated the consistency and accuracy of IMFPs determined from comparison of the intensity of elastically reflected electrons with theoretical calculations. The scatter in determined IMFPs with experimental geometry, spectrometer energy resolution and the procedure for background subtraction was determined. Four spectrometers with widely different geometries and energy resolutions, placed in four different laboratories in three countries were used. Four background subtraction methods (Shirley, linear, Tougaard, and ELPSEP) were applied to isolate the elastic peak intensity from the reflected electron spectra. The RMS deviation of the IMFP from a function fitted to the data is 3.01 - 4.11 A depending on the background subtraction method and it is smallest for the Tougaard method. The RMS deviation from IMFP values calculated by Tanuma et al is 3.41 - 4.41 A again with the smallest value for the Tougaard method. The mean percentage deviation from the Tanuma et al values is ~ 18 %. The results point to the conclusion that the major contribution to the inaccuracies in IMFPs determined with the elastic peak method is not the background subtraction procedure but rather lack of accuracy of the presently available models for elastic electron scattering, i.e. atomic elastic scattering cross sections and effects of crystallinity that are not included in the presently applied models. @FootnoteText@ @footnote@ Work supported by EU contract INCO COPERNICUS ERBIC15CT960800.

4:40pm MC-TuA9 Measurement of Silicon Dioxide Film Thicknesses by XPS, *C.J. Powell*, National Institute of Standards and Technology; *A. Jablonski*, Polish Academy of Sciences

It is now customary for the effects of elastic-electron scattering to be ignored in measurements of overlayer thicknesses by XPS. It is known, however, that elastic scattering can cause the effective attenuation length (EAL), needed for the thickness measurement,@footnote 1@ to be appreciably different from the corresponding inelastic mean free path.@footnote 2@ We have investigated the effects of elastic-electron scattering in measurements of the thicknesses of SiO@sub 2@ films on Si from XPS measurements with Al and Mg K@alpha@ x rays. Calculations have been made of substrate and oxide Si 2p photoelectron currents for different oxide thicknesses and emission angles using an algorithm based on the transport approximation.@footnote 3@ This algorithm accounts for the occurrence of elastic scattering along electron trajectories in the solid. It was found that the average EAL, determined from the substrate currents with and without an oxide overlayer of a certain thickness, varied weakly with oxide thickness and emission angle for a restricted range of emission angles. For emission angles greater than about 60°, corrections need to be made to this average EAL in order to determine the oxide thickness. These corrections will be described.@FootnoteText@ @footnote 1@A. Jablonski and C. J. Powell, Surf. Interface Anal. 20, 771 (1993). @footnote 2@A. Jablonski and C. J. Powell, J. Electron Spectrosc. 100, 137 (1999).

@footnote 3@I. S. Tilinin, J. Zemek, and S. Hucek, Surf. Interface Anal. 25, 683 (1997).

5:00pm MC-TuA10 A New Angle on Angle Dependent XPS, K.S. Robinson, G. Jones, R. White, J. Wolstenholme, VG Scientific, UK

Angle dependent XPS offers the ability to determine relative distributions, compositions and layer thickness for layers thinner than the XPS analysis depth. In practice, the use of angle dependent XPS is limited by the need to acquire data at several angles, usually requiring the sample to be tilted. The analysis of small features is also difficult because tilting the sample changes the analysis area as the projected shapes of the X-ray spot and / or analysis area on the sample change. We previously presented results@footnote 1@ from a commercial instrument where the electron input lens could be used to sequentially define two angles; a surface sensitive angle and a bulk sensitive angle, allowing angle dependent XPS without moving the sample. This method has now been extended to allow simultaneous collection of angle dependent XPS data from a range of angles. We present data from this instrument which shows the application to oxide thickness measurements and more complex structures. @FootnoteText@@footnote 1@QSA-10 at University of Surrey, UK, 1998.

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