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 σ 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.

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

Quantification & Accuracy in Surface Analysis
Moderator: C.R. Brundle, Applied Materials

2:00pm **AS-MoA1 Toward a Comprehensive Quantitative Workbench for Surface Analysis**, ***R.A. Weller***, Vanderbilt University **INVITED**

I will address issues in the application of symbolic computation to surface analysis. Until quite recently, the most important factors affecting the style of technical software have been the limitations imposed by the speed and storage capacity of contemporary computing hardware. In retrospect, while understandable in the context of the times, this linkage has produced computational tools that lack generality, are inflexible, or that must be frequently updated because of evolving computer hardware or operating system software. The seeds of an alternative approach have been sown by the authors of modern tools for general-purpose symbolic mathematical computation, where fundamental considerations argue for hardware independence and the generality of algorithms. Symbolic computation is a revolutionary computing technology. Mathematics is an exercise in discovering patterns and manipulating symbols according to complex and exceedingly numerous, but well defined and self-consistent rules. When advances in computer speed and memory capacity made it possible to store and implement these rules automatically, the stage was set for a revolution on a scale comparable to the revolution produced by automatic numerical computation five decades ago. Some implications of this revolution for the field of surface analysis will be presented, through examples drawn from medium energy backscattering spectrometry, four-point probe measurements, and radiation effects in semiconductors. The distinctive properties of an extensible surface analyst's quantitative workbench will be discussed. An important conclusion is that most technical software now being written should be based on robust algorithms and fidelity to correct physics without (much) regard for the characteristics of the hardware on which it will initially be implemented.

This work has been supported in part by the U.S. Army Research Office through grant DAAD 19-99-1-0283.

2:40pm **AS-MoA3 Quantitative XPS and the Morphology Problem : Simple Algorithm for the Amount of Substance at the Surface**, ***S. Tougaard***, University of Southern Denmark

It is well known that due to electron attenuation, the measured XPS-peak intensity depends strongly on the in-depth atom distribution. Quantification based only on the peak intensity leads therefore to huge uncertainties. The problem was basically solved by developing models for the detailed analysis of the energy distribution of emitted electrons leading to algorithms summarized in.[1] These algorithms have been extensively tested experimentally and found to be able to determine the morphology of surfaces with quite high accuracy.[2] Practical application of these algorithms has increased after ready to use software packages were made available[3] and they are now being used in labs worldwide. These software packages are easy to use but they need operator interaction. They are not well suited for automatic data processing and there is an additional need for simplified strategies that can be automated. In this paper we report on a very simple algorithm that takes the morphology effect into account. It is a slightly more accurate version of the algorithm previously proposed by Tougaard (eq.(8) in[4]). Although it was proposed more than a decade ago, the practical applications of this simple formula has not previously been studied in any great detail. The algorithm gives the amount of atoms within the outermost 3 IMFPs with a good accuracy and it also gives a rough estimate for the in-depth morphology. The validity of the simple algorithm is tested on several experimental systems and the results are compared to analysis of the same samples quantified by more accurate methods.

[1] S. Tougaard, J. Vac. Sci. Technol. A14, 1415 (1996)
[2] S. Tougaard, Surf. Interf. Anal. 26, 249 (1998)
[3] S. Tougaard: QUASES-Tougaard, Software package for Quantitative Analysis of Surfaces by Electron Spectroscopy, Ver 5.0 (see: www.quases.com).
[4] S. Tougaard, J. Vac. Sci. Technol. A8, 2197 (1990).

3:00pm **AS-MoA4 The Information Depth and the Mean Escape Depth in Auger Electron Spectroscopy and X-ray Photoelectron Spectroscopy**, ***A. Jablonski***, Polish Academy of Sciences, Poland, *C.J. Powell*, National Institute of Standards and Technology

The information depth (ID) is a measure of the sampling depth for the detected signal in Auger-electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) while the mean escape depth (MED) is a measure of surface sensitivity. We report ID and MED calculations for Si 2s, Si $2p_{3/2}$, Cu 2s, Cu $2p_{3/2}$, Au 4s, and Au $4f_{7/2}$ photoelectrons excited by Mg Kα x rays. Similar calculations were made for Si L_3VV, Si $KL_{23}L_{23}$, Cu M_3VV, Cu L_3VV, Au N_7VV, and Au $M_5N_{67}N_{67}$ Auger transitions. The ID and MEDs were derived from an analytical expression for the electron depth distribution function obtained from a solution of the kinetic Boltzmann equation within the transport approximation. The ratios of the IDs and the MEDs to the corresponding values found if elastic-electron scattering effects were negligible, R_{ID} and R_{MED}, were less than unity and varied slowly with electron emission angle α for emission angles less than 50^o. For larger emission angles, these ratios increased rapidly with α. For $\alpha \leq 50^o$, average values of R_{ID} and R_{MED} varied linearly with the single-scattering albedo, ω, a simple measure of the strength of elastic scattering effects. For $\alpha = 70^o$ and $\alpha = 80^o$, R_{ID} also varied linearly with ω but R_{MED} showed a quadratic variation. As a result of elastic scattering of the signal electrons, AES and XPS measurements at $\alpha = 80^o$ are less surface-sensitive than would be expected if elastic scattering had been neglected. Conversely, AES and XPS measurements made for $\alpha \leq 50^o$ are more surface sensitive as a result of elastic-scattering effects.

3:20pm **AS-MoA5 Wavelets: A New Technique for Spectral Processing in Surface Science - Applications to Filtering and Deconvoluting HREELS and XPS Data**, *C. Charles, J.P. Rasson, G. Leclerc, P. Louette*, ***J.J. Pireaux***, Facultés Universitaires Notre-Dame de la Paix, Belgium

Last decade has witnessed the emergence of new powerful signal analysis tools: the wavelet transform is one of them.[1] By simultaneously taking into account both the time and frequency domains, a wavelet analysis is a priori more efficient and covers a larger spectrum of applications than the Fourier Transform. The wavelet theory will be briefly presented, with comparison to Fourier analysis. Three applications for HREELS (High Resolution Electron Energy Loss Spectroscopy) and XPS (X-Ray Photoelectron Spectroscopy) will follow: noise filtering, peak detection and deconvolution. We first use synthetic data, a quite common practice in statistics: the correct answer is indeed known; it is thus possible to assess the validity and robustness of the algorithms, under clear hypotheses; errors can be calculated. The filtering algorithm proceeds with an original 'Local in Time and Frequency Translation Invariant Poisson Smoothing' code, that adapts itself to a spectrum containing peaks of very different amplitudes. Regions with a local maximum is then automatically detected with wavelets, allowing a Localized Least Squares method to precisely locate and determine the intensity of a peak. Different applications on real HREELS and XPS data are illustrated; they are particularly encouraging.

[1] I. Daubechies, Ten lectures on wavelets. Philadelphia, PA, SIAM, 1992

3:40pm **AS-MoA6 Ultra Thin SiO_2 on Si: Quantification of the Oxide Thickness and Carbonaceous Contamination**, ***M.P. Seah***, *S.J. Spencer*, National Physical Laboratory, UK

An analysis is made of the quantification issues in the measurement of ultra-thin layers of SiO_2 and of carbonaceous contamination on (100) and (111) polished Si surfaces. For the analysis of the oxide thickness, a simple equation is generally used involving two parameters; the attenuation length of photoelectrons in the oxide, L, and the ratio, R_o, of the intensities of the Si 2p peak from bulk thermal SiO_2 and from pure Si. An analysis of previously reported measurements of L gives an average value of only 6% less than the theoretical value. However, careful measurements of R_o, via two routes, indicate consistently that a value of 0.88 ± 0.05 should be used rather than the calculated value of 0.53 ± 0.05. This difference may arise through systematic errors in the values for the relevant inelastic mean free paths, the silicon dioxide density and the shake-up intensity contributions. Previously reported experimental values of R_o range from 0.67 to 0.87. Sources of uncertainty in these parameters and in the thickness will be addressed. Measurements of a basis set of materials for an international study, started in March 2002 under the auspices of the Consultative Committee for Amount of Substance (CCQM), show average correlations with ellipsometry better than 0.13 nm over the thickness range 2 nm to 8 nm. Measurements of the carbonaceous contamination show how to clean and store the samples effectively and the relevant parameters for a consistent carbon quantification.

4:00pm **AS-MoA7 Correcting for Detector-Induced Non Linearity in Photoelectron Spectroscopy Counting Systems**, ***C.S. Fadley***, *N. Mannella, S. Marchesini*, University of California at Davis, *A. Kay*, Intel Corporation, *S.-H. Yang*, IBM Almaden Research Center, *S. Mun*, Intel Corporation, *M.A. van Hove*, Lawrence Berkeley National Laboratory

The photoelectron intensity levels reached in exciting surfaces with both laboratory sources and third-generation synchrotron radiation can in many cases exceed the linear response range of the final detection system involved.[1] For example, the quantitative analysis of complex oxides via core-level intensities has been found to be strongly influenced by this non-linearity,[2] as have angle-resolved valence spectra[3] and magnetic dichroism measurements on magnetic systems.[2] Experiments involving resonant photoemission, in which the photon energy is scanned through an absorption edge, are also strongly affected.[4] In this paper, we demonstrate two quantitatively accurate procedures to correct for such non-linearity effects. The first method directly yields the detector efficiency by measuring a flat-background reference intensity as a function of incident x-ray flux, while the second method determines the detector response from an analysis of broad-scan survey spectra at different incident x-ray fluxes. Although we will use one spectrometer system (the Scienta ES200) as an example, the methodologies discussed here should be useful for many other cases. This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences Division, under Contract No. DE-AC03-76SF00098.

[1] M.P. Seah, M. Tosa, Surf. Interface. Anal. 18 (1992) 240; (b) M.P. Seah, I.S. Gilmore, S.J. Spencer, J. Electron Spectrosc. 104 (1999) 73-89.

[2] P. Wernet, N. Mannella et al., to be published.

[3] D. Dessau and Y. Chuang, private communication.

[4] A. Kay, Ph.D. Thesis, University of California Davis, 1998; A.W. Kay et al., Physical Review B 63, 115119,U214-U222 (2001) and references therein.

4:20pm **AS-MoA8 Theoretical Foundations of Surface Stress Measurements using Atomic Force Microscope Cantilevers**, ***J.E. Sader***, The University of Melbourne, Australia

Due to its extreme sensitivity and speed, the atomic force microscope (AFM) has recently emerged as an important tool in the measurement of surface stress. Fundamental to this application is theoretical knowledge of the effects of surface stress on the deflections of AFM cantilever plates. This is normally obtained by use of Stoney's equation, which is derived for a completely unrestrained plate. In this talk, the validity of Stoney's equation to rectangular and V-shaped AFM cantilever plates is investigated. It is found that use of Stoney's equation can lead to significant errors in measurements made using AFM cantilevers. Detailed finite element results and new analytical formulae, which replace Stoney's equation and greatly improve on its accuracy, shall be presented.

4:40pm **AS-MoA9 Elementary and Structure Analysis of Si Wafers and Thin Films by Using an X-ray Waveguide-Resonator**, ***V.K. Egorov***, *E.V. Egorov*, Russian Academy of Science (IPMT RAS), Russia

Analysis of composition and structure for Si wafers surface and thin films is carried out at X-ray beam grazing incidence (TXRF, GIRD). The methods fulfillment requires creation of an X-ray line beam with small width, low divergence and high radiation density. Monochromatization of the beam is nonobligatory demand. Such X-ray beam is formed indeed by planar X-ray waveguide-resonator (PXWR).[1] PXWR is the narrow extensive slit formed by two planes polished dielectric reflectors. The slit size must fall into the certain size interval. At quartz reflectors intervals for Mo$K\alpha$ and Cu$K\alpha$ are limited by sizes: 15-45 nm and 15-95 nm. Waveguides capture radiation in the angle aperture $\Delta\theta<2\theta_c$, where θ_c is the total reflection critical angle. Realistic emergent beams have width 50-100 nm, hight 1-10 mm, divergence $\Delta\theta<2\theta_c$ and radiation density exceeded one in standard formed beam systems by 3-4 orders. Composite PXWR has the emergent beam divergence $\Delta\theta<<2\theta_c$ at preservation of a total intensity. Schemes of diffractive and spectroscopic devices equipped by PXWR are considered. Data for X-ray beam diffraction on thin films at its grazing incidence and for focusing scattering scheme are presented. There are discussed X-ray fluorescence spectra collected at the grazing incidence on film targets of beams formed by PXWR. The model for the spectrum treatment taking into account PXWR using for the target excitation is formulated. PXWR application leads to falling of element detection limit more than one order in comparison of the standard TXRF spectrometer scheme. TXRF device with PXWR is more cheap, more simple in exploitation. PXWR can be used for TXRF study of Si wafers with d>300 mm and adapted for "in situ" measurements.

[1] V.K. Egorov, E.V. Egorov, T.V. Bil'chik, Investigation in Russia, v3, pp. 423-441 (2002). http://zhurnal.ape.relarn.ru/articles/2002/040e.pdf.

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

Polymer Characterization
Moderator: J.E. Fulghum, Kent State University

8:20am **AS-TuM1 Chemical Bonding of Perfluoropolyether End Group with Carbon Overcoat Surface by Irradiating Visible Laser Light**, ***L. Zhu***, *J. Zhang, T. Liew, K. Ye,* Data Storage Institute, Singapore

A thin lubricant film was applied on a magnetic hard disk carbon overcoat to reduce friction force, resist corrosion and minimize wear. Further treatment of the lubricant is to improve one or more of its properties for its compatibility with increasing magnetic recording densities. In this paper, we investigate the chemical bonding of perfluoropolyether lubricant molecules with carbon overcoat surface by irradiating visible laser light. A Nd:YAG laser with a wavelength of 532nm was used to irradiate the lubricant film (2 nm) on carbon overcoat surface in ambient environment. Samples were analyzed using the time-of-flight secondary ion mass spectroscopy. We found that with increasing laser energy, the ion yield of the end group CF2CH2OH decreases indicating the formation of chemical bonds of the end group with the active sites on the carbon overcoat surface. Secondary ion mapping of the laser irradiated area shows that fluorine and backbone fragments COF2 and C2OF4 are concentrated in the bonding area. This is in sharp contrast with our previous results with UV laser irradiation on the lubricant where the abundance of the end group remains almost constant with increasing laser energy and two unique backbone peaks are generated, indicating direct scission of the lubricant molecules in UV regime.

8:40am **AS-TuM2 TOF-HREELS and AFM Characterization of Highly Oriented Teflon (PTFE) Films**, ***Z. Yang***, *G. Bernhardt, R.L. Jackson, L.J. LeGore, P. Kleban, W.N. Unertl, B.G. Frederick*, University of Maine

Highly oriented polytetrafluoroethylene (PTFE) films are potentially useful as substrates for anisotropic growth of organic and bio-materials and as model surfaces for studying surface modification. High resolution electron energy loss spectroscopy (HREELS) has advantages of surface specificity, sensitivity and the possibility of non-dipolar interaction mechanisms, but has required relatively long data acquisition times. We have developed a novel time-of-flight (TOF-HREELS) spectrometer, which utilizes a throughput advantage to dramatically reduce acquisition times.[1] PTFE films were deposited onto sputtered films of gold and platinum on oxide-covered Si wafers by the friction transfer process.[2] The samples were studied by AFM to characterize the film roughness and thickness. The AFM images reveal long, straight ribbons of PTFE parallel to each other when deposited at a substrate temperature of 220 °C and a pressure of 1kg/8 mm^2. Comparisons are made between HREELS spectra obtained by the conventional instrument and the TOF-HREELS spectrometer.

[1] R. H. Jackson, et al., Surf. Sci. (2002), in press; L. J. LeGore, et al., ibid.

[2] P. Bodö, M. Schott, Thin Solid Films 286 (1996) 98.

9:00am **AS-TuM3 Surface Analysis of Poly (dimethylsiloxane) using Time-of-Flight Secondary Ion Mass Spectrometry**, *J.A. Gardella,* ***R. Rey-Santos***, The State University of New York at Buffalo

The study of polymer surface structures has become an important topic in surface chemistry. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is one of the most powerful techniques for surface analysis. ToF-SIMS has been used to study the secondary and tertiary structures of polymers. The Langmuir-Blodgett technique has been used to prepare thin films of poly (dimethylsiloxane) (PDMS) monolayers. Reflection Absorption Fourier Transform Infrared Spectrophotometry (RA-FT-IR) has been used to identify the surface structure of PDMS films. The use of the statistical chain breaking model of poly (alkyl methacrylates) by Zimmerman, Hercules, and Benninghoven published in Analytical Chemistry in 1993, helped us to determine the statistical chain breaking model for PDMS. Our goal is to use polymers as model systems to investigate the ion formation mechanisms and provide information about the long-range forces between polymer chains.

9:20am **AS-TuM4 Surface Analysis of Novel PDMS-Containing Amphiphilic Graft Copolymer by X-Ray Photoelectron Spectroscopy**, ***L. Chen***, *P.L. Valint, J.A. Gardella*, State University of New York at Buffalo

The surface composition of a series of amphiphilic graft copolymers consisting of hydrophilic poly(2-hydroxyethyl methacrylate) [poly(HEMA)] backbones and hydrophobic poly(dimethylsiloxane) (PDMS) side chains prepared by both photoinduced-radical and anionic polymerization techniques has been determined by angle dependent X-Ray Photoelectron Spectroscopy (XPS). The effects of PDMS graft length, PDMS bulk content and Molecular Weight Distribution (MWD) on the surface composition were investigated. It was found that the PDMS surface concentration increased with the increase of PDMS bulk content, but the effect of the bulk content on PDMS surface concentration for copolymers with long graft chains is much smaller than that for copolymers with short graft chains. For a given PDMS bulk content, a longer PDMS graft gave a surface richer in siloxane. The dominating factor in defining the siloxane surface segregation is not bulk content but graft length for these copolymers. PDMS surface concentration of copolymers with narrow MWD was observed higher than that with broad MWD, this could be explained by the purification process the copolymers went through during preparation.

9:40am **AS-TuM5 Embedding of Noble Metal Nanoclusters into Polymers as a Potential Probe of the Surface Glass Transition : Study with XPS**, ***V. Zaporojtchenko***, Christian-Albrechts University of Kiel, Germany

Embedding of noble metal nanoclusters into polymers is introduced as a novel method with a strong potential to follow the polymer glass transition at the surface.[1] X-ray photoelectron spectroscopy (XPS) in combination with transmission electron microscopy (TEM) was used to characterize the formation of nanoclusters during the noble metals (Au and Cu) deposition onto different polymers and to study the embedding of nanoclusters into polymers. The size of the metallic clusters and an embedding depth were determined using a mathematical correction of the XPS intensity.[2] This procedure is based on the measurement of the ratio of two XPS lines of the same metal with different binding energies and their attenuation length. X-ray photoelectron spectroscopy (XPS) has been applied to study the embedding of Cu and Au nanoclusters into polycarbonate, nylon as well as polystyrene films with different molecular weight by annealing the polymer films above the glass transition temperature Tg . It is shown that the temperature dependence of the embedding depth is clearly correlated to the glass-transition temperature of the polymer. Our investigations strongly support a depression of Tg at the surface compared with that of the polymer bulk. This supports the view that the molecular motion is enhanced near the surface due to the additional degrees of freedom. The enhancement of the surface glass transition temperature was observed due to Ar ion treatment of the polymers. The changes of Tg , which are qualitatively related to cross-linking, depend on the ion fluencies in the range of 10E13 - 10E14 cm^{-2} .

[1] V. Zaporojtchenko, T. Struskus, J. Erichsen, F. Faupel, Macromolecules 34(5) (2001) 1125.

[2] V. Zaporojtchenko, K. Behnke, T. Struskus, F. Faupel, Surf. Interface Anal. 30 (2000) 439.

10:00am **AS-TuM6 Surface Composition in Isotopic Polymer Mixtures Based on ToF-SIMS and Neutron Reflectivity**, *A. Takahara, D. Kawaguchi,* ***K. Tanaka***, Kyushu University, Japan, *S. Tasaki,* Kyoto University, Japan, *M. Tozu, T. Hoshi,* Ulvac-Phi, Inc., Japan, *T. Kajiyama*, Kyushu University, Japan

Surface composition in blend films composed of monodisperse polystyrene (hPS) with the number-average molecular weight, Mn, of 19.7k and deuterated monodisperse polystyrene (dPS) with Mn of 847k was examined by time-of-flight secondary ion mass spectroscopy (ToF-SIMS) in conjunction with neutron reflectivity (NR). Although hPS has higher surface energy than dPS, ToF-SIMS and NR revealed that hPS was enriched at the outermost surface of the films. The surface segregation of hPS can be accounted for by the molecular weight disparity for both components, that is, an entropic effect.

10:20am **AS-TuM7 SPM Structural Study of Phase Segregation, Thermal Behavior, and Aging of Poly(Ester Urethane) Compression Molded Samples**, ***M.E. Hawley***, *E.B. Orler, D.A. Wrobleski, R.P. Hjelm*, Los Alamos National Laboratory

Only a limited number of structural studies have been performed on segmented poly urethanes using tapping mode scanning probe techniques to determine both the nanostructure and the corresponding nanophase segregation of hard and soft segments within the samples. This type of information is needed to better understand the mechanical and thermal properties of these materials and to facilitate modeling efforts. In order to address these issues, we have fabricated a compression molded segmented poly(ester ure thane) samples with varying hard (HS) to soft segment (SS) ratios. Samples were examined using scanning probe phase imaging techniques to obtain the topography and map the corresponding HS and SS segregation before and after heating to over 100 °C both ex-situ and in-situ to and correlate those results with thermal absorption data. Changes in structure were followed as a function of time to address aging issues. A number of significant differences were observed before and after these thermal plastic sampl es were heat treated. Variations in structure and heat-induced morphological changes were directly related to HS content. Fine 10 to 10 nm thick lamellar- or fibril-like structures were most prominent in samples with lower HS content while harder, thicker elongated structures seen to a limited extent on all samples dominated the surface of high HS samples. The disappearance of the fine structures appears to be related to a peak in the endothermal data. The reappeared emanating from the large rod-like structures first as short branching then completely covering the surface after less than 2 days. Surface roughness increased in the process by approximately 10x.

10:40am **AS-TuM8 Surface-induced Ordering of Poly(ethylene terephthalate) Studied with In-situ Grazing Incidence X-ray Diffraction**, ***J.E. Macdonald***, *M. Durell, D. Trolley,* Cardiff University, UK, *P.C. Jukes, A.M. Higgins, R.A.L. Jones*, University of Sheffield, UK

Grazing incidence x-ray diffraction has been performed during in-situ annealing of a polymer thin film for the first time to investigate the molecular configuration at the surface of poly(ethylene terephthalate) (PET) films during crystallisation. The structural ordering at the surface of the film was compared directly with that in the bulk of the film by employing incident angles at and above the critical angle for total reflection. Ordering was observed at the surface at annealing temperatures of 85-95°C, while the bulk of the film remained amorphous. Parallel in-situ atomic force microscopy studies give direct images of the spherulites formed at the surface. Both techniques in tandem thus yield the structure and kinetics of ordering at the surface and in the bulk of the film.

11:00am **AS-TuM9 A Novel Micromechanical Platform to Measure the Surface Stress Produced by Electroactive Polymers**, ***V. Tabard-Cossa***, *M. Godin, O. Laroche, B. Seivewright,* McGill University, Canada, *A. Badia,* Universite de Montreal, Canada, *B. Lennox, P. Grutter*, McGill University, Canada

A novel platform to measure the surface stress produced by ionic electroactive polymer (EAP) materials is presented. In order for these materials to be used as conventional microactuators, it is important to accurately characterize them and, in particular, quantify the surface stress associated with the applied potential, so that their mechanical limitations and advantages can be determined. Micromechanical cantilever-based sensors, with their high sensitivity and fast response, are ideal tools for the characterization of these molecular scale electromechanical actuators. A standard, three-probe, electrochemical system is used, with an Ag/AgCl reference electrode and a Pt counter electrode, in a combined apparatus with a surface stress AFM cantilever-based sensor, where the cantilever simultaneously serves as the working electrode to obtain surface stress data in parallel with cyclic voltammetry (CV). The instrument, capable of integrating the electrochemical setup with the surface stress sensor requirements, will be described. The experimental setup, with the optimal cell geometry, necessary electronics and required software and hardware components will be shown. Dodecyl benzenesulfonate-doped polypyrrole (PPy(DBS)) in an aqueous solution of Na(DBS) is the EAP studied. Potentiostatic growth results of polypyrrole films on gold coated AFM cantilevers and their characterization by cyclic voltammetry and AFM/SEM will be presented. In addition, bending of the PPy/Au coated cantilever bilayer structure is measured as a function of applied potential. The equation used to calculate the surface stress induced during cyclic voltammograms circumvents the need to know the cantilever's Young's modulus by using readily measurable cantilever properties.[1] Finally, surface stress as a function of applied potential will be shown and its correlation with oxidation and reduction peaks addressed.

[1] M. Godin et al., Appl. Phys. Lett. 79, 4 (2001).

11:20am **AS-TuM10 Photoelectron Spectroscopy of Conjugated Polymers**, *R. Friedlein,* Linköping University, Sweden, *S.L. Sorensen,* Lund University, Sweden, *W. Osikowicz, M.P. de Jong,* ***W.R. Salaneck***, Linköping University, Sweden **INVITED**

Conjugated polymers have been studied by photoelectron spectroscopy and other related surface science techniques for over two decades. In the past few years, however, several advances have been made in classical techniques. Some aspects of X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS), as applied to conjugated polymers, will be hi-lighted. New results on high quality conjugated polymers will be presented.

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.[1] 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 amp-hours. 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.

[1] H. 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 $E := Y/\sigma$ 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 $\Delta l \sim (1/E)^{\text{Â½}}$. 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^+, Au_1^+, Au_2^+ and Au_3^+. 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_{Ga}) 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, δr, 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 Cazaux[1]) 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/CrO_2 on indium-tin-oxide. 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.

[1] J. 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 X-ray 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 (~10^6 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 SiO_2 is comparable to an uncovered metal line. Numerical studies suggest that the bias voltage necessary to minimize the edge-contrast 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).

Applied Surface Science
Room: Exhibit Hall B2 - Session AS-TuP

Topics in Applied Surface Science

AS-TuP1 Observation of Preferably Electrical Activation of Boron Implanted at Low Energy by Scanning Capacitance Microscopy, ***M.-N. Chang***, National Nano Device Laboratories, Taiwan R.O.C., *D.-H. Deng*, National Tsing Hua University, Taiwan R.O.C., *C.-Y. Chen*, National Nano Device Laboratories, Taiwan R.O.C., *J.-H. Liang*, National Tsing Hua University, Taiwan R.O.C., *F.M. Pan*, National Nano Device Laboratories, Taiwan R.O.C.

Ultrashallow doping is one of the technical trends on ultra large-scale integrated circuit. Low energy ion implantation combined with rapid thermal annealing (RTA) is necessary to obtain required ultrashallow doping profiles. It is well known that scanning capacitance microscopy (SCM) is a promising technique providing two-dimensional (2D) doping profiles. In this work, we have provided a new method employing plane view SCM images to investigate the lateral carrier distribution in ultrashallow p$^+$ junctions formed by BF$_2^+$ implantation at low energies. RTA processes were performed at 550, 850 and 1050 °C for different anneal times from 5 to 120 seconds in N$_2$ ambient. The width and pitch of the designed grating pattern are 0.8 and 2 µm, respectively. The SCM image clearly shows the existence of a transition region at each pattern edge of which the width reveals the carrier concentration gradient of the lateral p-n junction. For the same anneal time, the sample annealed at 850 °C exhibits a wider transition region than the one at 1050 °C, indicating that more electrically active boron atoms can be obtained at higher anneal temperatures. The SCM signal intensity, i.e., dC/dV, is a function of the free carrier concentration of the implanted region. Comparing the dC/dV profiles across the implantation pattern for the samples treated under different RTA conditions, one can find that less implanted boron atoms at the pattern edge are electrically activated than at the center region. According to this study, the edge effect will significantly affect the lateral carrier concentration distribution upon RTA processes when the pattern size decreases.

AS-TuP2 Development of a Large Area XPS Imaging Instrument, *T. Tazawa, M. Kato, M. Kudo,* ***Y. Iijima***, *K. Tsutsumi*, JEOL Ltd., Japan

Recently, the photoelectron image measurement by XPS has become a very general surface analysis method. However, the measurement over the whole sample surface is very difficult because the measurable image region by the micro analysis in XPS is small. We developed an XPS instrument which is able to measure the region covering from 30x30µm^2 to 50x18mm^2. The photoelectron image measuring method is the stage scanning method. The minimum image resolution of this instrument is 30µmm or less. For this instrument, a newly designed magnetic lens was developed to achieve a better performance than the static lens system. This magnetic lens to measure a micro area is placed under the sample stage. In addition, the X and Y axes of sample stage can be operated by an accuracy of 1µm. The maximum operation ranges of the X and Y axes are 0-50mm and 0-18mm, and they are controlled by a PC system. We obtained photoelectron images of a polymer surface and a hard disk surface with this XPS instrument, polymer surface and hard disk surface. The results show that the large area XPS imaging analysis is very effective in the measurement of element distribution and chemical states of the sample surface by surface analysis. So we can say this instrument as "Chemical state image XPS". Moreover, the total reflection XPS (TRXPS) measurement function was added to this XPS instrument. TRXPS is a new surface analysis method, has sensitivity several times higher than XPS in surface analysis of the semiconductor such as Si wafers.

AS-TuP3 Compensating for the Ubiquitous Hydrocarbon Overlayer to Enable Quantification of the Elemental Composition from XPS; the Air-formed Film at the Aluminium Surface, *M.R. Alexander, G.E. Thompson,* ***X. Zhou***, UMIST, UK, *G. Beamson*, Daresbury Laboratories, UK

Air-formed and anodic films at the surface of aluminium are of considerable technological importance. The chemistry of the surface is relevant to the performance of coated and bonded aluminium; XPS is a powerful tool in characterising this surface.[1] Unfortunately, when an overlayer of hydrocarbon contamination is present on the air-formed oxide film, quantification of the elemental composition using XPS requires a correction to account for the greater attenuation of lower KE photoelectrons. Different methods have been developed to correct for this effect that do not require etching or angle resolved measurements. These include the Ebel model and modifications of this approach,[2] the Evans approach[3] and the Vereecke and Rouxhet method.[4] Application of these methods is compared for a range of overlayer thickness using a plasma polymerised hexane coating (ppHex) as a model for hydrocarbon contamination. The thickness was measured using in situ quartz crystal microbalance, XPS signal attenuation and TEM. A stable and reproducible hydrothermally-formed pseudoboehmite (AlOOH) sample is used with hydrocarbon contamination as low as [C]=1 at%.[5] Application to relevant systems is considered.

[1] M. R. ALEXANDER, G. E. THOMPSON and G. BEAMSON, Surface and Interface Analysis 29 (2000) 468.

[2] M. EBEL, M. SCHMID and A. VOGEL, J Electron Spectroscopy and Related Phenomena 34 (1984) 313.

[3] S. EVANS, Surface and Interface Analysis 25 (1997) 924.

[4] G. VEREECKE and P. ROUXHET, Surface and Interface Analysis 27 (1999) 761.

[5] M. R. ALEXANDER, S. PAYAN and T. M. DUC, Surface and Interface Analysis 26 (1998) 961.

AS-TuP4 Multivariate ToF-SIMS Image Analysis of Patterned Protein Surfaces, ***B. Wickes***, *D.G. Castner*, University of Washington

Novel biomaterial surfaces are being developed to specifically interact with their biological environments. These surfaces are patterned with multiple species of biomolecules to generate regions of differing bioactivity. The chemical structure of these surfaces must be characterized at high spatial resolution. Static Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) imaging offers a modality for simultaneously visualizing the spatial distribution of multiple surface species. Because ToF-SIMS images yield a full mass spectrum at each pixel, it is possible to use characteristic mass fragments to identify and differentiate regions of different chemistry with a spatial resolution of approximately one micron. However, these datasets can be challenging to analyze because of their large size, complex chemistries and low ion counts per pixel. The combination of spectral data denoising and multivariate image analysis provides a convenient method to process ToF-SIMS images. Wavelet filtering followed by Principal Components Analysis (PCA) was applied to ToF-SIMS images. For example, the raw image data from a patterned poly(ethylene oxide) (PEO)-protein surface showed contrast in over 50 peaks; the resulting PCA model compressed the contrast from the raw data into two variables describing the variation between the protein- and PEO-regions, and the background and a defect region, respectively. Applying PCA to filtered image matrices removes user bias in peak selection and allows use of the full mass spectrum at each pixel. It highlights the peaks important in the chemical image and yields a new set of variables identifying the chemistries responsible for the image contrast.

AS-TuP5 Thermally Isolated Support Membrane for Low-noise Si JFET Amplifiers, ***Y. Bae***, *J. Podosek, M. Yun, J. Bock, K. Sukhatme, E. Jones*, Jet Propulsion Laboratory

A thermally isolated JFET module was fabricated at JPL to work with a high-sensitivity Bolometer that operates at a low temperature, ~300mK. The JFET module provides 24 differential pairs of JFETs, which need be warmed to 130K to provide optimal noise performance, 7nV/rtHz. Each channel has 2 feedback resistors and source, drain, gate, etc. electrical leads. However, power from the JFET electronics is dissipated on the 10K helium vapor-cooled stage of the Herschel cryostat, and the dissipation needs to be minimized to not affect the hold time and temperature of the liquid-helium. Although the JFETs are capable of satisfying the noise and power requirements, the design of the thermal isolation stage dominates the thermal dissipation requirement and presents a significant design challenge. We have devised a novel suspended nitride membrane to provide thermal isolation while satisfying the vibration and thermal cycle environment of a cryogenic space borne instrument. The JFET module needs to meet Bolometer's setup requirements: 1) a voltage noise performance less than 7nV/rtHz/JFET and 2) heat dissipation less than 3.5mW/module. Siliconix U401 JFET differential amplifiers must be heated to 130K to meet the 7nV/rtHz noise requirement. The silicon nitride membrane acts as a 2-D heat flow, so minimizing its thermal conductance is best achieved by reducing the membrane thickness or perforating the membrane. We present tests of the thermal conductance of several membrane architectures, and have carried out through testing of a complete 1.8micron silicon nitride assembly populated with JFET dies. The complete JFET module was characterized in functions of the power and voltage noise. The module passed shock environment test, 15g 400 - 2500Hz sine sweep, and passed thermal cycling to 77K, however it exceeded the heat dissipation requirement. Our test data on thinner membranes indicates we can meet the dissipation requirement with a 1.0micron membrane.

AS-TuP6 Non-destructive Depth Profiling Analysis of Surface Oxidation of b-FeSi$_2$ Thin Film on Si (100) by SR-XPS, ***T. Saito***, *H. Yamamoto, K. Yamaguchi*, Japan Atomic Energy Research Institute, *M. Haraguchi*, Ibaraki University, Japan, *T. Nakanoya*, Japan Atomic Energy Research Institute, *M. Imamura, N. Matsubayashi, T. Tanaka, H. Shimada*, National Institute of Advanced Industrial Science and Technology, Japan, *K. Hojou*, Japan Atomic Energy Research Institute

The formation process of iron silicid (β-FeSi$_2$) films on Si single crystal surfaces has been extensively studied because of their excellent characters as semiconductors. It is well known that stable β-FeSi$_2$ films are not oxidized even under ambient atmospheres. However, the oxidation behaviors of the topmost surface layer of β-FeSi$_2$ are not well understood. In the present study, we investigated the surface oxidation of β-FeSi$_2$ thin films formed on a Si (100) surface by means of synchrotron radiation X-ray photoelectron spectroscopy (SR-XPS) to obtain the information on the surface chemical state and the depth distribution of chemical components. The β-FeSi$_2$ films (10 - 100 nm) were formed by ion beam sputter deposition method (IBSD) or solid phase epitaxy method (SPE) at a substrate temperature of 973 K. After formation of β-FeSi$_2$ phases, the samples were exposed to oxygen or air at room temperature. SR-XPS depth-profiling analyses revealed formation of β-FeSi$_2$ islands on the substrates. The comparison of experimental results with simulation results using inelastic mean free paths (IMFP) of photo-electrons in Si and Fe revealed that about 50 - 70 % of the substrates surface were covered by β-FeSi$_2$ phases. In addition, the topmost surface of β-FeSi$_2$ and exposed Si substrates are almost completely covered by uniform thin SiO$_2$ layers. The thicknesses of the oxide layers were estimated at about 1.0 nm. These results indicated that thin surface SiO$_2$ layers behaved as a protective layer for further oxidation of β-FeSi$_2$ surfaces.

AS-TuP7 Surface Characterisation of Fluorinated Polyether Ionomers from Aqueous Dispersions, ***R. Canteri***, *G. Speranza, M. Anderle*, ITC-irst Centre for Scientific and Technological Research, Italy, *S. Turri, S. Radice*, Ausimont Spa Research & Development Centre, Italy

The introduction of perfluoropolyether (PFPE) bifunctional macromers, in polyurethane coatings[1,2] has lead to a substantial improvement of the durability characteristics and surface properties of the material, while maintaining the advantage of an easy application technology in a variety of environmental conditions and temperatures.[3] In this work we present a surface characterisation by TOF-SIMS and XPS of a new series of polymer thin films containing PFPE macromers, applied in form of PolyUrethane Aqueous Dispersions (PUAD). In fact, environmental issues are forcing the development of waterborne polymer systems (dispersions or emulsions) in order to reduce the problems of solvent emissions in the atmosphere. The PUAD systems presented in this work can be defined as polyurethane ionomers, since self-dispersion in water is achieved by using co-monomers containing a NR$_3$ or a -COOH group, which can be salified with acids or bases. It is known that many of the performances of the coating, like low surface energy (water and oil repellence), lubrication and low friction etc, are related to the capability of fluorinated structures to stay close to the polymer-air interface. The analysis of the outermost layer of the dried waterborne coatings by TOF-SIMS is compared with analyses by XPS obtained at two different angles (90° and 15° take off angle) for sampling different thickness. These results are finally compared with those obtained on the solventborne crosslinked coatings[4] containing similar PFPE macromers.

[1] G. Simeone, S. Turri, M. Scicchitano, C. Tonelli, Angew. Makromol. Chem. 236 (1996) 111.

[2] S. Turri, M. Scicchitano, G. Simeone, C. Tonelli, Progr. Org. Coat. 32 (1997) 205

[3] J. Scheirs, S. Burks, A. Locaspi, Trends Polym. Sci. 3 (1995) 74

[4] S. Turri, S. Radice, R. Canteri, G. Speranza and M. Anderle, Surface and Interface Analysis 29 (2000) 873.

AS-TuP8 A New Transparent Conducting Oxide: Indium Molybdenum Oxide (In$_2$O$_3$: Mo), ***Y. Yoshida***, Colorado School of Mines, *T.J. Coutts, T.A. Gessert*, National Renewable Energy Laboratory

We report our preliminary work on a new transparent conducting oxide, indium molybdenum oxide (IMO, 4% Mo), prepared by radio frequency magnetron sputtering (RF sputtering). Other works have recently reported that thermal reactive evaporated thin films of IMO showed an exceptionally high mobilities of 80 - 130 $cm^2 V^{-1} s^{-1}$.[1] To study further the functionality of molybdenum in IMO, and to test if the large-area deposition capability afforded by RF sputtering can produce high mobility, we produced In$_2$O$_3$ (IO) and IMO films in an argon and oxygen atmosphere at a substrate temperature of 350°C. Electrical properties were studied as a function of the ratio of oxygen to argon (O$_2$/Ar) from 0 to 1. We found that the best film properties resulted when a small O$_2$/Ar ratio was used ($\leq$ 0.3). IMO films grown at 0.005 O$_2$/Ar achieved a mobility of 37.5 $cm^2 V^{-1} s^{-1}$, a carrier concentration of 1.16 x 10^{20} cm^{-3}, a resistivity of 5 x 10^{-3} Ω-cm, and ~70% transmission in a visible range (400nm - 900nm). IO film quality was optimized at ~0.025 O$_2$/Ar, resulting in a mobility in the range of 20 - 30 $cm^2 V^{-1} s^{-1}$, carrier concentration of 2.03 x 10^{18} cm^{-3}, and resistivity of 9.98 x 10^{-2} Ω-cm. IMO films showed much better electrical properties than the undoped IO films grown under the same range of conditions. X-ray photoelectron spectroscopy (XPS) confirmed the presence of molybdenum 6+ in the films. X-ray diffraction (XRD) analysis confirmed phase purity in the films and possible texture changes due to variations of the amount of oxygen in the system.

[1] Y. Meng, X. Yang, H. Chen, J. Shen, Y. Jiang, Z. Zhang, Z. Hua, Thin Solid Films 394 (2001) 219.

AS-TuP9 SIMS Analysis of Copolymers: A Test for Statistical Ordering, *A.G. Shard*, University of Sheffield, UK, ***S. Clarke***, *M.C. Davies*, University of Nottingham, UK

Statistical copolymers of lactic and glycolic acids (PLGA) have been investigated by SIMS. The composition of the copolymer can be determined through analysis of the intensities of secondary ions which contain several monomer units, as described previously for non-statistical copolymers.[1] We describe here a method for determining whether the SIMS data are consistent with the copolymer being statistical. This method is applicable to any copolymer, the only requirement being the detection of secondary ions containing two or more monomer units. This information is used to determine the relative ion yields of selected secondary ions in the SIMS spectra of PLGA and the invariance of ion yields across a large composition range is shown, validating our previous work.

[1] Shard AG, Davies MC, Li X, Volland C, Kissel T, Macromolecules 30, 3051, 1997.

AS-TuP10 Impurity Dopant Profile Measurement and its Quantitative Analysis using Nano Capacitance-Voltage (NCV) Method, ***E.-S. Kang***, *H.-J. Hwang*, Chung-Ang University, Korea, *G.-Y. Lee*, Samchok National University, Korea

It is well known that commercial scanning capacitance microscope (SCM) systems are not easy to obtain the local dC/dV curves over the dopant range of 1020 - 1018cm-3 because of smaller depleted volume charges generated under the surface by SCM tip size. This problem will prevent us from acquiring quantitative carrier depth information correctly. To do this, it needs the developing of robust capacitance sensor and the more powerful SCM modeling. For the more accurate inverted dopant profile in higher dopant area, therefore, we have added some factors such as SCM tip/sample interaction and fully calculated volume charges into previous modeling parameters. In addition, we have developed a new capacitance sensor operating about 1.7GHz frequency bandwidth. The capacitance sensor used in commercial SCM has been using the amplitude modulation method. However, we have taken the frequency modulation technique for increasing the accuracy in higher dopant area. This new capacitance sensor consists of a voltage-controlled oscillator with controlled voltage, a microstrip resonator, and a RF mixer IC and PLL (Phased-Lock Loop) for detecting the capacitance variations. We have called this system Nano Capacitance-Voltage (NCV). This technique will bring a greater enhancement for the current SCM sensitivity and performance.

AS-TuP11 A Quantitative Comparison between Rutherford Backscattering and Time-of-Flight Medium Energy Backscattering, *B.R. Rogers*, ***R.D. Geil***, *Z. Song, D.W. Crunkelton, R.A. Weller, V. Pawar*, Vanderbilt University

Both conventional Rutherford backscattering (RBS) and time-of-flight medium energy backscattering (ToF-MEBS) have been used to determine the thickness and stoichiometry of thin dielectric films (Al$_2$O$_3$) deposited on silicon, and a comparison is made between the two ion beam techniques. The characterization of these films is important in optimizing the deposition process and ultimately the film properties. The conventional RBS and ToF-MEBS systems are capable of 1.8 MeV and 270 keV He$^+$ beams, respectively. ToF-MEBS is a lower energy derivative of conventional RBS that offers improved depth resolution and sensitivity at the expense of total analyzable depth and ease of use.[1] Channeling was performed with both systems to suppress the substrate signal and enhance the signal from the thin dielectric film. Grazing angle analysis was performed with the RBS system to increase particle path length in the sample, thereby improving depth resolution. It was found that for films less than about 200 Å RBS had little sensitivity to the thin Al$_2$O$_3$ films while ToF-MEBS detected Al and O in films that were tens of angstroms in thickness.

[1] Weller, Robert A. Introduction to Medium-Energy Ion Beam Analysis. Methods in Materials Research (2000) 12b.1.

AS-TuP12 SIMS Depth Profiling of Multilayer Structures, ***A. Godines***, *Yu. Kudriavtsev, A. Villegas, R. Asomoza*, CINVESTAV-IPN, Mexico

In this work we performed a comparative study of the depth resolution function for metal and semiconductor multi-layers in depends on primary ion kind, primary ion energy and angle of incidence. Influence of oxygen flooding on the depth resolution was analyzed as well. Subject of our study was different test semiconductor multi-layers grown by MBE: AlAs/GaAs, AlGaAs/GaAs, GaAsN/GaAs, InGaAs/GaAs, AlGaN/AlN, as well as metal multi-layers (neutron super-mirrors): Co/Ti and Si/Fe. The number of layers has varied from 20 to 200; the thickness of an individual layer has varied from 1 monolayer to about 20nm. Sputtering was performed by cesium and oxygen positive ions. SIMS depth resolution depends on many different factors and effects such as surface roughness and surface roughness caused by ion bombardment, ion mixing effect, radiation enhanced diffusion and so on. In our work the ion mixing was found as the main effect affecting the depth resolution of semiconductor multi-layers. Parameter, which characterizes it, was found being proportional to the root square of the primary ion energy, normalized on the cosine of the angle of incidence, for both metal and semiconductor multi-layers. We did not find any mass dependence of the depth resolution that is in a contrast with the ballistic mixing model. Oxygen ion bombardment leaded to a dramatic reduce of the depth resolution in the case of metal multi-layers, because of a strong surface roughness formation. Moreover, a strong matrix effect was found at the interfaces of metal layers, which was more pronounced in the case of cesium ion bombardment. In order to reduce the matrix effect, we applied the oxygen flooding. This technique: Cs+ ion bombardment with CsM+ (where M is the analyzed element) secondary ions monitoring and with simultaneous oxygen flooding was found as the best method for metal multi-layer depth profiling.

AS-TuP13 Sample Topography Developed by Sputtering in Cameca Instruments: an AFM and SEM Study, *E. Iacob*, *M. Bersani, A. Lui, L. Vanzetti, D. Giubertoni, M. Barozzi, M. Anderle*, ITC-irst, Italy

Secondary ion mass spectrometry (SIMS) is based on ion sputtering. Removing atoms layer by layer we can get a satisfactory depth distribution analysis. To obtain a suitable depth resolution for semiconductors applications low impact energy and glancing angles are mandatory. However high dose ion bombardments results in a change of surface topography causing problems in quantitative analysis and depth resolution deterioration. The morphological artefacts on the crater surface, depend on various SIMS sputtering parameters and samples conditions. The induced morphology by ion sputtering require detailed characterization. In this work we analysed, by using of Atomic Force (AFM) and Scanning Electron (SEM) Microscopies, the morphological effects induced by ion bombardment on various samples: monocristalline Si <100>, polycrystalline Si and amorphous silicon oxide. Topographic irregularities, induced by SIMS analysis are studied showing the dependence on sputtering condition. We used different instruments (Cameca Sc-Ultra and Cameca 4f) comparing the effect of analytical conditions as impact angle, incidental ion species, ion dose and impact energy. The goal is to determine best parameters to minimize roughness and surface irregularities considering or not the employment of the sample stage rotation.

AS-TuP14 Comparison of Experimental Protocol for Low Energy Sputter Yield Measurements of Advanced Materials as a Function of Sputtering Angle, *V.S. Smentkowski*, General Electric - Global Research Center, *S. Hu*, Lockheed Martin

We will report two different experimental protocol that can be used to measure the sputter yield of advanced materials as a function of sputtering angle. One protocol uses standard surface analytical instrumentation while the second protocol utilizes a home built system containing a broad-beam (Kaufman) ion source. Low energy (350 eV and below) Xe was used for all measurements. When the samples were sputtered at normal incidence, the data generated using the two protocol agreed, however as the sputtering angle increased a divergence was noted in the data sets. It will be demonstrated that the divergence correlates with a change in the surface topography, which biases the data generated using one of the protocol. As part of this study, we measured the sputtering yield of silicone dioxide thin films obtained from different vendors and noted that the yield varied. Possible explanations for this effect will be reported. We believe that effects such as these are partially responsible for the lack of agreement in other sputter yield measurements reported in the literature.

AS-TuP15 Mathematical Topographical Correction of XPS Images using Multivariate Statistical Methods, *K. Artyushkova*, *S. Pylypenko, J.E. Fulghum*, Kent State University

For rough heterogeneous samples, the contrast observed in XPS images may result from both changes in elemental or chemical composition and sample topography. Background subtraction is frequently utilized to minimize topographic effects so that images represent concentration variations in the sample. For this purpose, background images are recorded at slightly lower and/or higher binding energies than the main peak for all species of interest. Background-corrected images result from subtracting a background energy map from one acquired at the peak energy. This procedure may significantly increase the data acquisition time. Multivariate statistical methods can assist in resolving topographical and chemical information from images. Principal Component Analysis (PCA) is one method for identification of the highest correlation/variation between the images. Topography which is common to all of the images will be resolved in the 1st most significant component. The score of this component contains spatial information about the topography of the surface, while the loading is a quantitative representation of the topography contribution to each elemental/chemical image. Reconstructing the data using the score and loading for the 1st component will provide mathematical background images. These images, which contain the topographical information for all elemental/chemical images, can be used to correct the images for topography in the same way the experimental background images are used, thereby reducing the time required for data acquisition. The mathematical background correction scheme is developed and validated by comparing results to the experimental background correction for three samples with differing degrees of topography. The first example is a very rough, fossilized sample, the second is a patterned sample with roughness on the order of the XPS sampling depth and the third is a flat polymer blend sample. This work has been partially supported by NSF CHE-0113724.

AS-TuP16 High Spatial Resolution XPS Analysis of Si Samples Prepared using the FIB Lift-out Technique, *J. Fenton*, *A. Ferryman, J.E. Fulghum*, Kent State University, *L.A. Giannuzzi*, University of Central Florida, *F.A. Stevie*, North Carolina State University

The goal of this project is to assess Ga+ contamination on Si in order to elucidate artifacts due to focused ion beam (FIB) milling. The FIB instrument has witnessed an increase in use from machining and processing to specimen preparation. However, the surface chemistry alterations, gallium implantation damage region, and residual effects of FIB sample preparation are not well understood. It is imperative that we understand the chemical and morphological alterations that this instrument may cause to its target, if correct interpretations regarding structure/property relationships of materials are to be made. FIB is currently most often used to prepare samples for microscopic techniques such as TEM, which have a higher spatial resolution than most surface analysis methods. Improvements in imaging and small area analyses have made X-ray photoelectron spectroscopy (XPS) an increasingly useful characterization technique for such samples, however. Utilizing spectra-from-images capabilities enables the acquisition of spectra from areas of ~ 1 micron in diameter, allowing for surface chemical characterization of FIB lift-out samples. This poster will discuss the use of XPS imaging and small area spectroscopy to characterize surface oxidation and Ga contamination in Si (100) prepared by the FIB lift-out method.

AS-TuP17 Elucidation of Three-Dimensional Structure in Polymer Blends using Correlated Confocal Microscopy and XPS Imaging, *L.A. Broadwater*, *K. Artyushkova, I. Smalyukh, O. Lavrentovich, J.E. Fulghum*, Kent State University

The complexity of heterogeneous polymeric materials makes it difficult to distinguish between alternative morphologies using a single analytical technique. Knowledge of both polymer surface chemistry and component distribution with depth can be important. In this study, blends of poly(vinyl chloride) (PVC) and poly(methyl methacrylate) (PMMA) have been investigated using confocal microscopy and imaging XPS. Confocal microscopy provides the distribution of phase separated areas as a function of depth (on a scale of microns), while XPS provides the surface distribution of phase separated regions. Conclusions based upon these comparisons will be compared to previous work from our group using imaging FTIR. This has been partially supported by NSF ALCOM and NSF CHE-0113724.

AS-TuP18 Correlative XPS and AFM: Chemical Phase Identification in Polymers, *J. Farrar*, *K. Artyushkova, J.E. Fulghum*, Kent State University

AFM can be utilized to provide both topographical and phase contrast information from polymeric materials. AFM phase contrast images potentially contain chemical information, although image interpretation can be challenging. XPS images contain chemical phase information, but at a significantly different spatial resolution. In this study we evaluate methods for the correlation of images with varying spatial resolutions, focusing on XPS and AFM. Processing for image correlation includes resizing, image alignment and resolution matching. Following imaging processing, classification methods are used to correlate components present in XPS and AFM images. Data from a variety of polymer samples will be used to demonstrate that classification of XPS and AFM images can be used to identify chemical phases in AFM images. This work has been partially supported by NSF ALCOM (DMR89-20147) and NSF CHE-0113724.

AS-TuP19 Surface Studies of Corrosion of Stainless Steel by Lead-Bismuth Eutectic, ***A.L. Johnson***, *D. Koury, B. Hosterman, D. Parsons,* University of Nevada, Las Vegas, *D. Perry,* Lawrence Berkeley National Laboratory, *J. Farley*, University of Nevada, Las Vegas

The corrosion of stainless steel by lead-bismuth eutectic (LBE) has been studied using various types of surface analysis, including Scanning Electron Microscopy (SEM) and X-ray Photoelectron Spectrometry (XPS). The goal is to understand the chemical react ion products and chemical reactions involves in the corrosion. The atomic composition of steel samples has been examined as a function of position. Sputter depth profiling has been employed to study the atomic composition as a function of depth. High resolution XPS studies reveal the oxidation state of the various elements. We have examined both unexposed steel samples and steel samples that have been exposed to LBE for various lengths of time for different temperatures. Crucial differences between the un exposed and exposed samples are demonstrated in the data. For example, nickel is present at the surface of the unexposed samples, but absent from the exposed samples. The latest experimental results will be presented and mechanistic implications discussed. This work was supported by the U. S. Department of Energy under the AAA UPP Program (UNLV) and Contract Number DE-AC03-76SF00098 (LBNL).

AS-TuP20 Initial Tests of a Draft Protocol for Wide Scan XPS Measurements, ***M.H. Engelhard***, *D.R. Baer*, Pacific Northwest National Laboratory

In May 2002 an international workshop on developing an expert XPS system was held in St. Malo, France. One output of that workshop, developed by a task group lead by Prof. James Castle, was a draft protocol for collecting a maximum amount of information from wide scan data. Although similar to approaches already used in some laboratories, the protocol is significantly different than the default wide scan spectra for most instruments and suggests that a significant amount of information can be routinely extracted from wide scan data that is generally ignored or missed. Although parts of the draft protocol (step size, scan width and preliminary charge correction) are common practice for use of our Quantum 2000, other parts (energy resolution, analysis for layered structure) are different than our usual practice. This paper reports our preliminary experience in a manual application of the initial version of this draft protocol to "routine" samples in our laboratory.

This work was conducted in the Environmental Molecular Sciences Laboratory, a U. S. Department of Energy User Facility run by Battelle Memorial Institute.

AS-TuP21 Surface Characterization of Nanoparticles for Cast Dispersion Strengthened Metal Matrix Nanocomposites, ***A.L. Linsebigler***, *V.S. Smentkowski, T. Angeliu*, General Electric Global Research Center

Oxide dispersion strengthened (ODS) metal matrix composites possess very stable nano-particles that provide strength at elevated temperatures, but have found limited commercial application due to complex processing and cost constraints. Solidification processing has been pursued as one of the most cost effective and versatile methods to produce metal matrix composites. However, composites produced by casting have significant challenges in wetting the surface of an oxide particle by molten metal. Particle wetting can be influenced by physisorbed and chemisorbed surface species and oxide stoichiometry. Surface characterization studies have been conducted on as-received and heat-treated alumina nanoparticles by SEM, AES, TOF-SIMS, and TPD methods. The roles of adsorbed species and surface functionalization on the wetting and dispersion of these nanoparticles in metal alloy matrices will be discussed.

AS-TuP22 Basic Characterization of Arcing in Sputtering Targets, ***F.G. Tomasel***, *D. Carter, H. Walde, J.J. Gonzalez, G.A. Roche*, Advanced Energy, Inc.

Arcing in sputtering deposition is a very well known phenomenon that affects quality of thin films. Different strategies have been devised to reduce arcing during the deposition process. However, it is felt that there is still a need for a further description of the basics of arc formation. This article intends to contribute in this subject by presenting a detailed description of the formation and evolution of arcs. The study combines the spatial and time resolved results of ultra high-speed, single frame photographs with an electrical characterization of the current and voltage waveforms for arcs occurring on different sputtering targets. Elaborating on these data, we will present a possible explanation for the results observed.

AS-TuP23 Characterization of Plasma Source Ion Implanted Stainless Steel for High Voltage Applications, ***N.D. Theodore***, College of William and Mary, *C. Hernandez,* Jefferson Lab, *D.M. Manos,* College of William and Mary, *H.F. Dylla,* Jefferson Lab, *R. Moore,* University at Albany Institute for Materials, *T. Siggins*, Jefferson Lab

Properly modifying the surface of stainless steel to increase efficiency or output power is useful in high voltage electrical pieces seen especially in particle accelerators for research and medicine, high-power radar, DC electron guns, and high power microwave tube and waveguide systems. In this study, highly polished stainless steel test pieces were processed in our integrated PSII/PVD system, which is capable of implanting ions while simultaneously depositing high purity SiO_2. Previous studies have shown that the suppression of field emission is enhanced in harder, smoother surfaces, and that nitrogen-implanted stainless steel increases surface hardness. Our recent work has shown that the suppression of field emission increases by an order of magnitude in surface-processed samples.[1] This study compares the surface character of unprocessed stainless steel with nitrogen-implanted stainless steel and nitrogen-implanted, SiO_2-deposited stainless steel using electric field microscopy, atomic force microscopy, micro-hardness testing, and Auger electron spectroscopy. The relative effectiveness of various surface-processing methods in reducing field emission will also be discussed. This work supported by the US Dept. of Energy and the Office of Naval Research.

[1] C. K. Sinclair, et al. "Dramatic Reduction of DC Field Emission From Large Area Electrodes By Plasma Source Ion Implantation." Proceedings of the 2001 Particle Accelerator Conference.

AS-TuP24 Nano-scale Mapping of Surface-photo-voltage by Scanning Tunneling Microscope : Ag/Si(001), ***O. Takeuchi***, *S. Yoshida, H. Shigekawa*, University of Tsukuba, CREST, Japan

It has been a subject of great interest to investigate the nanoscale spatial distribution of surface photo voltage (SPV) on semiconductor surfaces. In general, SPV measurement studies the change in band bending at semiconductor interfaces as a function of the external illumination, which offers information about local band diagram including band gap structure and mid-gap confined states as well as local density, diffusion length and lifetime of carriers. Thus, measurement of SPV with high spatial resolution opens a way for precise control of defect and dopant density in a specific nanostructure and investigation of its characteristics. In this study, we have mapped the nano-variation of SPV for partially covered Ag/Si(001) system with conventional scanning tunneling microscope (STM) from OMICRON, in UHV at 300 K and 80 K. To measure SPV, current-voltage curve (IV curve) measurement was performed while 2 mW HeCd laser beam was focused onto tunneling gap with mechanical chopping at 20 Hz. The spot diameter was about 0.1 mm. Since, the obtained IV curve gives the IV curves on dark and illuminated conditions simultaneously, SPV can be retrieved as lateral displacement of the two IV curves as a function of bias voltage. Spatial mapping was realized by performing the SPV measurement in grid points during conventional STM topograph imaging. Clear dependence of SPV on the distance from the two-dimensional Ag islands as well as linear dependence of SPV on bias voltage with static tunnel gap distance was observed.

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

Optical Methods and High-k Dielectrics Characterization
Moderator: H.G. Tompkins

8:20am **AS-WeM1 Verification of Silicon Native Oxide Growth Models using Spectroscopic Ellipsometry**, ***D.W. Crunkleton***, *V. Pawar, Z. Song, R.D. Geil, B.R. Rogers*, Vanderbilt University

The need for atomically clean silicon surfaces in microelectronics processing has lead to several proposed kinetic models of native oxide growth on silicon. In this work, we present new data sets from which these models are analyzed. We have measured the room temperature silicon dioxide growth on Si (100) samples pre-treated with various fluoride, chloride, and hydroxide base etchants. The oxide thickness is determined with multiangle spectroscopic ellipsometry. Many of the proposed kinetic models fit the trends in our data well; yet several tend to underestimate the final native oxide thickness.

8:40am **AS-WeM2 Measurement of Semi-Isolated Poly-Silicon Gate Structure with Optical Critical Dimension Technique**, ***D. Shivaprasad***, *J. Hu, M. Tabet, R. Hoobler,* Nanometrics, Inc., *W. Liu, H. Sasano, C. Bencher, D. Mui*, Applied Materials

The ITRS predicts the production of sub-100 nm transistor gates by 2004 pushing further the limit of the size and speed posed by 180 nm gates which are currently in use. With decreases in gate length, it has become extremely critical to measure these dimensions accurately using non-destructive techniques. Optical Critical Dimension (OCD) measurements are emerging as one of the most promising CD measurement techniques for sub-0.1 micron device fabrication. Compared to CD-SEM and X-SEM, OCD measurements are non-destructive, relatively high throughput, sensitive to sidewall profiles, and sensitive to sub-100nm linewidths. In the OCD technique, a broadband polarized light beam is focused onto the grating surface, and the spectrum of the 0th order reflection is measured. The spectrum contains a signature of the grating profile that is analyzed in real time using Rigorous Coupled Wave Analysis (RCWA). The real time curve fitting algorithms, which do not require library generation, make the analysis simple and easy to extend to a variety of grating structures. Since the OCD technique is based on specular diffraction, a primary requirement for the OCD measurement target is to have periodical grating structures with a line to space ratio typically 1:5. In this paper, we report using the OCD technique to measure poly-silicon gate grating with line to space ratio as large as 1:20. Poly-silicon gate grating structures with critical dimensions of 30â€”40 nm were measured with line to space ratios of 1:10 and 1:20. In both cases, the measurement showed excellent sensitivity to linewidth variations and detailed profile changes, without deterioration of repeatability. Data from an un-cleaned wafer with the hard mask still remaining will also be presented. This study has significantly extended the measurement range of the OCD technique and its application to isolated line measurements.

9:00am **AS-WeM3 Progress in Spectroscopic Ellipsometry: Applications from Vacuum Ultraviolet to Infrared**, ***J.N. Hilfiker***, *C.L. Bungay, R.A. Synowicki, T.E. Tiwald, C.M. Herzinger, B. Johs, G. Pribil, J.A. Woollam*, J. A. Woollam Co., Inc. **INVITED**

Spectroscopic ellipsometry (SE) is a non-contact and non-destructive optical technique for thin film characterization. In the past ten years, it has migrated from the research laboratory into the semiconductor, data storage, display, communication, and optical coating industries. The wide acceptance of SE is a result of its flexibility to measure most material types: dielectrics, semiconductors, metals, superconductors, polymers, biological coatings, and even multi-layers of these materials. Measurement of anisotropic materials has also made huge strides in recent years. Traditional SE measurements cover the ultraviolet, visible, and near infrared wavelengths. This spectral range is now acquired within seconds with high accuracy due to innovative optical configurations and new CCD detection. In addition, the wavelength range has recently been expanded both into the vacuum ultraviolet (VUV) and the mid infrared. This wide spectral coverage was achieved by utilizing new optical elements and detections systems, along with UV or FTIR light sources. Modern instrumentation is now available with unprecedented flexibility promoting a new range of possible applications. For example, the VUV spectral region is uniquely capable of characterizing lithographic materials for 157nm photolithography. The VUV also provides increased sensitivity for thin layers (e.g. gate oxides or self-assembled monolayers) and allows investigation of high-energy electronic transitions. The infrared spectral region contains new information about semiconductor doping concentration, phonon absorption, and molecular bond vibrations. In this work, we review the latest progress in spectroscopic ellipsometry hardware and software. Areas of significant application in both research and industrial fields will also be surveyed.

9:40am **AS-WeM5 Application of Bragg Light Scattering Method for Studying of Spatial Dispersion Effects in Ferroelectrics**, ***F.R. Akhmedzhanov***, Samarkand State University, Uzbekistan

Bragg light scattering method for studying of spatial dispersion effects was applied to pure $LiNbO_3$ and Mg doped $LiNbO_3$ ferroelectrics. The examined samples of pure $LiNbO_3$ and $LiNbO_3$ with Mg impurity (10^{-2} mol. %) were oriented along the axis of the third order with the accuracy of $10'$. Piezoelectric transducers of Lithium Niobate of appropriate cuts are used in order to excite the plane-polarized transverse acoustic waves with the frequencies of 0.4-1.5 GHz. Measurements of the dependence of the scattered light intensity from the distance to the piezotransducer along the direction of the acoustic wave propagation have been carried out in automatic regime. The scattered light intensity can be presented as function dependence of the light intensity I with respect to distance Z of acoustic wave shift: $I = I_0 \exp(-A*Z) \mathrm{Cos}^2(D*Z + F)$, Here I_0 is the scattered light intensity near piezotransducer, A is the attenuation coefficient of the acoustic wave, D - the specific rotation angle of the polarization vector and F - the initial phase angle. The obtained values of the scattered light intensities have been used to calculate the quantity and frequency dependence of the attenuation and of the specific rotation of polarization vector in given acoustic wave by modeling of above-mentioned equation. The effective constants of acoustical activity along the investigated direction were determined from the experimental data simultaneously. There has been shown the high efficiency and trustworthiness of the results of simultaneous calculation of attenuation coefficient and specific rotation of the polarization plane in gyrotropic crystals, as well as possibility of speculation of experimental curves by varying factors, which are changed in a real experiment.

10:00am **AS-WeM6 Titanium Dioxide Thin Film Growth on Si(111) by Chemical Vapor Deposition of Titanium(IV) Isopropoxide**, ***A. Sandell***, Uppsala University, Sweden, *M.P. Andersson,* Lund University, Sweden, *Y. Alfredsson,* Uppsala University, Sweden, *M.K.-J. Johansson,* Lund University, Sweden, *J. Schnadt, H. Rensmo, H. Siegbahn,* Uppsala University, Sweden, *P. Uvdal*, Lund University, Sweden

Due to its high dielectric constant, TiO_2 has been considered as a gate insulator material in Si-based MOSFETs, either in pure form or mixed with other compounds. In this contribution, I present a study of the initial stages of TiO_2 growth on Si(111)-(7x7) under ultra-high vacuum conditions using core level photoelectron spectroscopy (PES), x-ray absorption spectroscopy (XAS) and scanning tunneling microscopy (STM). The TiO_2 film was formed by means of chemical vapor deposition of titanium(IV) isopropoxide at a sample temperature of 500 C. The thickness and composition of the amorphous interface layer and its subsequent transition to crystalline anatase TiO_2 are discussed. Three different stages are identified: In the initial stage (film thickness <1 nm), the oxygen atoms are coordinated mainly to Si atoms giving rise to Ti atoms with oxidation states lower than 4+. The next stage (<3 nm) is best described as an amorphous $TiSi_xO_y$ compound in which the oxidation state of Ti is 4+ and the x and y values vary monotonically with the film thickness. Finally (>3 nm) a stoichiometric TiO_2 layer starts to form. The TiO_2 phase is anatase and the layer consists of largely equidimensional particles, approximately 10 nm wide. In addition, I will also broach the differences that occur upon lowering the growth temperature to 300 C and how the properties of the film can be altered by pre-oxidation of the Si(111)-(7x7) surface.

10:20am **AS-WeM7 Nitrided Silicon-Silicon Dioxide Interface: Electrical and Physico-Chemical Characterization by Complementary Surface Techniques**, ***L. Vanzetti***, *E. Iacob, M. Barozzi, D. Giubertoni, M. Bersani, M. Anderle,* ITC-irst, Italy, *P. Bacciaglia, B. Crivelli, M.L. Polignano, M.E. Vitali*, ST Microelectronics, Italy

The scaling down of MOS devices into the submicron regime needs high-quality ultrathin gate dielectrics. Silicon oxide nitridation is widely used to improve oxide reliability and to reduce interface degradation induced by electrical stress. Analytical issues in this field include electrical characterisation, nitrogen quantitative depth distribution and chemical characterisation. In this work NO and N_2O nitrided oxide layers with thicknesses in the range 70-120Å were studied. Different analytical techniques were used, namely the Elymat (Electrolytic Metal Tracer), SIMS and XPS. Surface recombination velocity was obtained from photocurrent measurements by a modification of the Elymat technique allowing the control of surface potential. The so-obtained surface recombination velocity was shown to be directly related to the interface state density of the as-grown oxide. Surface recombination velocity was correlated with nitrogen content in the silicon oxide layer, obtained by SIMS measurements. XPS analyses allow to explain the different electrical behaviour. In fact XPS measurements provide a complete chemical characterisation of these interfaces. In addition a comparison between quantified SIMS depth profiles and XPS etch-back depth profiles shows very good agreement in nitrogen profile shape and quantification. This approach results very effective for the full characterisation of this type of materials.

10:40am **AS-WeM8 Accurate SIMS analysis of SiON Films**, ***S. Miwa***, *H. Kobayashi*, SONY Corp., Japan, *K. Nakajima, K. Kimura*, Kyoto University, Japan

Oxynitride (SiON) films are generally used in advanced CMOS LSIs as gate dielectrics instead of SiO_2 films. The nitrogen distribution in the SiON films strongly affects the performance of the transistors, so it is important to analyze exact nitrogen profiles. Secondary Ion Mass spectrometry is the most frequently used method for the analysis of SiON films. In the analysis, low-energy Cs primary ions and the very high incidence angle (about 80 degrees from the normal incidence) are recommended to avoid knock-on, atomic mixing, and matrix effect over the SiON/Si structure. On the other hands, secondary ion yield is sensitive for the surface concentration of primary ion species. In this case, the surface coverage of Cs is dramatically varied depending on the slight change of the incidence angle because the incidence angle of primary ions is very high. We have carefully investigated that the angle dependence of relative sensitive factors (RSF) and the sputtering rate around this very high incidence angle. We have found that RSF is varied about 10% when the angle changed by 0.3 degrees and that sputtering rate is varied about 10% when the angle changed by 0.5 degrees. In conclusion, the incidence angle of primary ions must be controlled within only 0.1 degree in order to keep the quantification errors within 5%. We can control the angles well reproducibly by means of monitoring the ratio of the intensities of two secondary ions ($SiCs^+$ and Cs_2^+). We have also compared the N concentration obtained by SIMS with that obtained by High-resolution Rutherford Backscattering Spectrometry.

Biomaterials
Room: C-201 - Session BI+AS-WeM

Ambient Surface Science Techniques
Moderator: M. Grunze, Heidelberg Universität, Germany

8:20am **BI+AS-WeM1 A Challenging Problem: Interfaces between Condensed Matter**, ***M. Buck***, StAndrews University, UK **INVITED**

Surface Science has developed a zoo of techniques which allow the characterization of chemistry and structures of surfaces and adsorbates at an impressive level of molecular detail. Unfortunately, the large variety of available techniques dramatically reduces when dealing with systems under non-vacuum environment and, therefore, an understanding on a molecular level is much harder to gain. In addition to problems on the technical side, the situation is further complicated by the fact that "real world" interfaces are, in general, more complex compared to systems studied in surface science, e.g. larger molecular entities with more conformational degrees of freedom, amorphous structures, and additional interactions due to the environment. The talk discusses various routes to unravel the relationship between structures and properties of biomaterials interfaces and highlights problems and possible pitfalls associated with the investigation of such type of interfaces.

9:00am **BI+AS-WeM3 Surface Chemistry of Environmentally Relevant Transition Metal Oxides Studied in Aqueous Solutions using Soft X-ray Spectromicroscopy**, ***B.P. Tonner***, *K. Pecher*, University of Central Florida

The surface chemistry of environmentally relevant inorganic oxides can now be reliably assessed in solution, with high spatial resolution, using a methodology based on x-ray absorption spectroscopy with microfocussing.[1,2] A crucial aspect of this research is that the studies are performed in the presence of a complete water layer, with control of parameters such as buffer concentrations, dissolved oxygen content, and pH. We have concentrated on the fate of Fe and Mn oxides in mineral model compounds, and in addition important nano-scale materials like the 'green rusts.' Spatial chemical inhomogeneities are prevalent in such nano-scale minerals, and are revealed by x-ray spectro-microscopy "chemical state mapping." The state of these studies has matured to the point where chemical intermediates, formed as a result of microbial metabolism, can be reliably detected and identified. This paper will emphasize the quantitative aspects of performing assays of surface transition metal oxide valence distributions using L-edge spectromicroscopy.

[1] Rothe, J., E.M. Kneedler, K.H. Pecher, B.P. Tonner, K.H. Nealson, T. Grundl, W. Meyer-Ilse, and T. Warwick, Journal of Synchrotron Radiation 6, 359-361 (1999).

[2] K. Pecher, E. Kneedler, J. Rothe, G. Meigs, T. Warwick, K. Nealson, and B. P. Tonner, X-ray Microscopy 1999, W. Meyer-Ilse, T. Warwick, and D. Attwood, ed., (American Institute of Physics, NY, 2000) p. 291-300.

9:20am **BI+AS-WeM4 Investigation of Protein Adsorption with Simultaneous Measurements of Atomic Force Microscope (AFM) and Quartz Crystal Microbalance (QCM)**, ***K.-H. Choi***, *J.-M. Friedt, F. Frederix, W. Laureyn, A. Campitelli, G. Borghs*, IMEC, Belgium

We have combined the tapping mode atomic force microscopy (AFM) and quartz crystal microbalance (QCM) for the direct investigation and characterization of protein adsorption on various metallic surfaces. The adsorption of proteins, such as human plasma fibrinogen, γ-globulin and collagen, onto the metal/QCM surface were monitored using both methods at the same time when varying the concentration of them. We present the AFM images that shows the surface changes and the adsorption scheme of proteins with molecular resolution according to the shift of resonant vibration frequency of the QCM. The combination of AFM with QCM and the simultaneous measurements of the bio molecule adsorption with two techniques provide us with not only the sensing and detection technique but also the means for understanding the adsorption schemes of bio molecules on the metal surface.

9:40am **BI+AS-WeM5 Real-time AFM Investigations of the Enzymatic Degradation of DNA-polymer Dendrimer Complexes**, ***S.J.B. Tendler***, *H.G. Abdelhady, C.J. Roberts, S. Allen, M.C. Davies, P.M. Williams*, University of Nottingham, UK

Fundamental to surface recognition strategies is the need to develop both interfaces and imaging methods that allow the investigation of biomolecular recognition processes in solution, in-real time. One such set of processes is the enzymatic degradation of DNA, both when naked and when protected by polymeric (bio)materials. This system has clinical relevance in that polyelectrolyte complexes between polyamidoamine (PAMAM) dendrimers and DNA have emerged as potential non-viral vectors for therapeutic DNA delivery. Hence methods for analyzing the ability of PAMAM dendrimers to protect the DNA from degradative enzymes are of clinical significance. Here we have applied atomic force microscopy (AFM) in liquid to visualize at the molecular scale and in real time, the effect of the enzyme DNase I on generation 4 PAMAM dendrimers complexed with DNA (G4-DNA). The formation of G4-DNA is observed to provide a degree of protection to the DNA, the level of which rises with increasing PAMAM dendrimer to DNA ratio and to a certain degree with the time allowed for complexes to form.

10:00am **BI+AS-WeM6 Interaction of Water with Protein Resistant Self-Assembled Monolayers: Neutron Reflectivity Measurements of Water Density in the Interphase Region**, ***D. Schwendel***, *T. Hayashi, A.J. Pertsin, R. Dahint*, University of Heidelberg, Germany, *R. Steitz*, Hahn-Meitner-Institut, Germany, *F. Schreiber*, University of Oxford, UK, *M. Grunze*, University of Heidelberg, Germany

The interfacial behavior of surfaces, colloids, and molecules with water plays a substantial role in surface science and other areas. It is, in particular, responsible for colloid stability, micelle formation, biomembrane fusion, and the resistance of materials against proteins from biological media. These materials are of crucial importance in biotechnology and biomedical applications. One type of such bicompatible surfaces is represented by self-assembled monolayers (SAMs) on Au and Ag composed of undecanethiolates terminated oligo(ethylene glycols), $(-O-CH2-CH2-)n$ (hereafter EGn). Neutron reflectivity measurements on protein resistant methoxy tri(ethylene glycol) (EG3-OMe) and hydroxy terminated hexa(ethylene glycol) (EG6-OH) undecanethiolate self-assembled monolayers (SAMs) in contact with deuterated water reveal the presence of an extended (~5 nm thick) water interphase with a noticeably reduced density (85-90 % of bulk water density). This result is in qualitative agreement with Grand canonical Monte Carlo simulations of water next to the SAM surface. For comparison, neutron reflectivity experiments have also been performed on non-functionalized hydrophobic octadecanethiolate and hydrophilic hydroxy terminated undecylthiolate SAMs. Additionally, neutron reflectivity measurements on protein resistant SAMs formed from hydroxy and methoxy terminated tri(ethylene glycol) (EG3-OH and EG3-OMe) against high concentrated protein solutions of BSA show that the free dissolved protein does not contact the surface but that it is repelled over a distance of few nm. The profiles strongly suggest a BSA depleted water layer at the SAM/bulk interface of 4 to 6 nm while BSA adsorption is observed for non-resistant propoxy terminated tri(ethylene glycol) (EG3-OPr).

10:40am **BI+AS-WeM8 Force Spectroscopy of Self-Assembled Monolayers Containing 'Sandwiched' Oligo(Ethylene Glycol) Interfaces on Gold under Electrolyte Solution**, ***G. Haehner***, *C. Dicke*, University of St Andrews, UK, *S. Herrwerth, W. Eck, M. Grunze*, University of Heidelberg, Germany

Non-specific interactions between biomolecules and (synthetic) organic surfaces, and in particular materials which are resistant to the adsorption of proteins from biological media, are of crucial importance to the fields of biomaterials, biosensors and medical devices. Chemically functionalized (charged and hydrophobic) scanning force microscope probes can mimic local structures of proteins and hence allow it to study the influence of these parameters on the overall observed interaction separately. Oligo(ethylene glycol) (OEG) terminated self-assembled monolayers on gold show high inertness towards the non-specific adsorption of proteins. The underlying mechanism, however, has not yet been resolved completely. It appears that water as well as hydronium and/or hydroxyl ions play a central role. In order to scrutinize the interaction, the accessibility of the OEG interface to molecules/ions from solution was varied. This was accomplished by the molecular structure: the functional (OEG) part was terminated with hydrophobic chains of different length resulting in 'sandwich'-film-structures. Force spectroscopy measurements on these layered structures with hydrophobic probes under electrolyte solution reveal the importance of the different contributing factors to the overall interaction.

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

High-k Dielectric Characterization
Moderator: B.R. Rogers, Vanderbilt University

2:00pm **AS-WeA1 Ultra-high Resolution AES Depth Profiling using a Masked Specimen Holder**, ***K. Satori***, *H. Kobayashi*, SONY Corporation, Japan, *K. Kimura, K. Nakajima*, Kyoto University, Japan

Auger electron spectroscopy (AES) using an instrument with coaxial geometry for an electron column and a cylindrical mirror analyzer (CMA) has the advantages of high sensitivity and accurate mapping capability. However, the analytical depth when using a coaxial CMA is larger than when using a hemispherical analyzer because the angle of the Auger electrons detected by a coaxial CMA ranges widely at any given tilt angle. This is a serious problem when we wish to evaluate ultra-thin films such as gate dielectrics. Some studies have been conducted using ion sputtering with low kinetic energy, to obtain high depth resolution. However, these studies have highlighted that one of the most important factors concerning depth resolution is the analytical depth. We designed angled and masked specimen holders to obtain a more shallow analytical depth using the coaxial CMA. We optimized the holder angle by calculating the distribution of the angle of the Auger electrons and the actual AES measurement to increase the intensity of the Auger electrons emitted at high angle from the surface normal. Next, we designed an electron shadow mask on a specimen holder to prevent the analyzer detecting the Auger electrons at low angle from the surface normal. Using the holder that we designed, the surface-sensitivity becomes three times higher than that of conventional methods. In addition, to improve depth resolution, we designed a new mask shape and obtained a low incident angle for the ion beam. Using the holder, the depth resolution was improved sufficiently to evaluate ultra-thin silicon oxynitride films (thickness 2.5nm). The shape of the AES depth profile was in good agreement with that obtained by means of high-resolution Rutherford backscattering spectroscopy. Our method is easy to use but useful for obtaining a shallow analytical depth and high depth resolution.

2:20pm **AS-WeA2 Sputtering Artifacts in Depth Profile Analysis of HfO_2 and $HfSi_xO_y$**, ***C.F.H. Gondran***, *J.A. Bennett, M.R. Beebe*, International SEMATECH

As electrical device sizes continue to shrink, thinner transistor gate oxides are required. Soon the required gate oxide thickness will be too thin to be obtained using SiO_2. Thicker gate oxides can be used to obtain the desired equivalent silicon dioxide thickness if the material used has a higher dielectric constant. HfO_2, ZrO_2 and their silicates are among the most promising candidates for alternative high-dielectric-constant gate materials. With these new materials, come a host of new challenges for both device processing and materials characterization. Preferential sputtering and other affects seen in the Auger and SIMS depth profiles of HfO_2 and $HfSi_xO_y$ result in the appearance of Hf deep into the Si Substrate. In mixed oxides the relative size of this artifact varies with the composition posing a challenge for quantitative analysis. The sputtering artifacts in HfO_2 and $HfSi_xO_y$ are characterized and practical approaches for analysis are discussed.

2:40pm **AS-WeA3 Challenges for the Characterization and Integration of High-k Gate Dielectrics**, ***R.M. Wallace***, University of North Texas **INVITED**

The integration of new high-k gate dielectric materials into advanced planar CMOS technology presents several significant challenges.[1] Moreover, the introduction of these materials is expected to occur at an unprecedented pace to meet industry technology forecasts[2] and will therefore mandate a rapid correlation of physical characterization with electrical performance. Although recent research has dwelled on the search for a material that yields a suitable (higher) dielectric constant, a more important problem is the actual integration of any new dielectric material in existing CMOS flows in a cost-effective manner. These integration issues include etching, control of phase segregation, dopant penetration, gate electrode compatibility, and many others that will influence the resultant electrical properties. This talk will examine several of these integration issues and the associated surface and thin film characterization challenges that must be addressed for successful high-k gate dielectric integration.

[1] For a review, see: G.D.Wilk, R.M.Wallace and J.M.Anthony, J. Appl. Phys. 89 (2001) 5243.

[2] See the International Technology Roadmap for Semiconductors at http://public.itrs.net/.

3:20pm **AS-WeA5 Quantitative Depth Profiling of Hafnium Films by Electron Spectroscopies**, ***P. Mrozek***, *H. Krasinski, D. Sarigiannis, B. Kraus*, Micron Technology Inc.

Surface analysis was performed by AES/XPS on hafnium oxide and hafnium oxy - nitride films grown on silicon. Depth profiles, using elastic peak intensities, aided estimates for inelastic mean free path ratios. Subsequent AES and XPS quantitative analysis was performed using matrix correction factors that incorporated these ratios. Linear least squares analysis was used to deconvolute the different chemical states from elastic peaks and to identify phases within multilayers. Auger parameter, based on hafnium high energy Auger transitions M4N6,7N6,7 and the deep 3d5/2 core level, was used to verify the presence of oxide and silicide layers that were detected by these hafnium chemical state profiles. The results were compared with those obtained from the usual AES quantitative analysis approach to demonstrate the value of supplemental elastic peak measurements.

3:40pm **AS-WeA6 Binding Energy Shifts in Soft X-ray Photoelectron Spectroscopy of $HfO_2/SiO_2/Si$ High-k Gate-dielectric Structures**, ***M.D. Ulrich***, *J.G. Hong, J.E. Rowe, G. Lucovsky*, North Carolina State University, *T.E. Madey*, Rutgers, The State University of New Jersey

We have observed binding energy shifts for thin films of $(HfO_2)_x(SiO_2)_{1-x}$ on Si(111) substrates deposited as alternative high-k gate dielectrics in the film thickness range, 6-15 Å. Thin films of HfO_2 and $(HfO_2)_x(SiO_2)_{1-x}$ on Si(111) substrates were prepared by remote plasma enhanced chemical vapor deposition (RPECVD). This process results in a 6-10 Å layer of SiO_2 between the deposited dielectric and substrate. Samples were analyzed using high-resolution soft X-ray photoelectron spectroscopy (SXPS) with synchrotron radiation. Photoemission measurements were performed at the National Synchrotron Light Source (NSLS) located at Brookhaven National Laboratories using beamline U4A which has a total instrumental resolution of better than 0.1 eV. The Si $2p_{3/2}$ [SiO_2] binding energy from SiO_2 films on silicon substrates decreases with decreasing (5-30 Å) film thickness due to core hole screening. This shift is well described with an image charge model of core hole screening.[1] According to this model, an overlayer above the SiO_2 layer should further increase Si $2p_{3/2}$ [SiO_2] core hole screening causing an additional decrease in binding energy. For the HfO_2 samples, SiO_2 thickness was determined to be ~10 Å. The Si $2p_{3/2}$ [SiO_2] binding energy was 0.3 eV lower than that of a SiO_2 film of similar thickness without the HfO_2 overlayer. The Si $2p_{3/2}$ single-component SXPS spectra indicate that interfacial silicate exists between the SiO_2 and HfO_2 with a signal strength less than one third that of the SiO_2 peak. The result of the Si $2p_{3/2}$ [SiO_2] binding energy matches the image charge model well.

[1] J. W. Keister, J. E. Rowe, J. J. Kolodziej, H. Niimi, H.-S. Tao, T. E. Madey, and G. Lucovsky, J. Vac. Sci. Technol. A 17, 1250 (1999).

4:00pm **AS-WeA7 Chlorine and Oxygen Transport in ALD Grown ZrO_2 and HfO_2 Films on Silicon**, ***S. Ferrari***, *G. Scarel, C. Wiemer, S. Spiga, M. Fanciulli*, Lab. MDM - INFM, Italy

ZrO_2 and HfO_2 have received a lot of attention as possible candidates to replace SiO_2 as insulating layers in CMOS structures. Oxygen diffusivity in those materials may affect a number of properties. Among them, oxygen stoichiometry in the oxide, interfacial silicon oxide formation/reduction are critical parameters that need to be controlled in order to succesfully build high-k based devices with the desired properties. The growth of ZrO_2 and HfO_2 films by means of Atomic Layer Deposition (ALD) from $ZrCl_4$ And $HfCl_2$ percursors is known to cause significant incorporation of chlorine. Chlorine may have detrimental effects on the electrical properties of the films, by introducing positive charge in the film and possibly localized states in the band gap. In this paper we study oxygen and chlorine diffusion by means of Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) in ZrO_2 and HfO_2 films as a function of annealing temperature in different environment gasses such as N_2 and O_2 . Preliminary results show that in oxygen deficient environment chlorine desorption in inhibited, demonstrating that chlorine can out-diffuse by exchange with the oxygen. HfO_2 shows a limited oxygen and chlorine mobility as compared to ZrO_2.

4:20pm **AS-WeA8 A Study of the Microstructure and Electrical Properties of the Reoxidized HfO_2 upon Annealing Methods**, ***D. Lee***, *H.-E. Seo, D.-H. Ko, M.-H. Cho*, Yonsei University, Korea, *C.-W. Yang*, Sungkyunkwan University, Korea

Hafnium oxide has been known as gate dielectric material to replace SiO_2 in MOS devices. First of all, for preparation of reoxidized HfO_2, Hf films were deposited on p-type Si(100) substrate by DC magnetron sputtering system. Next, Hf films were reoxidized by RTA(Rapid Thermal Annealing) and vertical furnace. They were analyzed by AFM, XRD, XPS, AES and HR-TEM. For ~50nm thick as-deposited Hf film, the HfO_2 layer was observed about ~5nm at the surface by HR-TEM. The HfO_2 layer increased to be ~15nm at 600°C in N_2 ambient. Especially, HfO_2 grains were shown not only at the surface of the Hf film but also at the silicide(Hf_5Si_4) grain boundaries. These grains of silicides on the Si substrate were not observed at the sample that annealed at 800°C for 30min in N_2 ambient, due to decompositing into HfO_2 and Si. And then the Si reacted with the oxygen that diffused from surface and accumulated on the interface of Si-substrate. For ~10nm thick as-deposited Hf films, it was observed that the HfO_2 films locally crystallized in the whole films and the interfacial layer between HfO_2 and Si substrate was about 8Å. After annealing by furnace as increasing anneal time and temperature in N_2 or O_2 ambient, also, the thickness of interfacial layer was increased to that of as-deposited film. As a result of measuring C-V and I-V, it was calculated that the value of CET was 51.5Å at -3V and dielectric constant was about 15.5 at 800°C for 5min in N_2 ambient. The leakage current of HfO_2 film decreased as the anneal temperature increased or time increased at constant temperature.

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

Practical Surface Science I
Moderator: R. Hull, University of Virginia

9:00am **AS-ThM3 Arrays of Chemomechanically Patterned Patches of Homogeneous and Mixed Monolayers of 1-Alkenes and Alcohols on Single Silicon Surfaces**, ***T.L. Niederhauser***, *Y.-Y. Lua, G. Jiang, S.D. Davis, R. Matheson,* Brigham Young University, *D.A. Hess, I.A. Mowat,* Charles Evans & Associates, *M.R. Linford*, Brigham Young University

We have demonstrated a facile, chemomechanical method of simultaneously functionalizing and patterning silicon with single organic monolayers by scribing it while it is wet with 1-alkenes,[1] 1-alkynes,[1] and 1-haloalkanes.[2] This method can be used to create different monolayer coatings in distinct and precisely controlled regions on an individual surface. Like microcontact printing, this technique allows multiple, patterned, surface features to be prepared with ease. To create these arrays a Si surface is 1) wet with a reactive compound, 2) scribed in a specific region with a computer-controlled diamond-tipped rod, 3) rinsed with a solvent, and 4) dried. Without moving the Si surface from its original position, this process is then repeated to create monolayer coatings in regions distinct from the first. With this technique we have prepared arrays of functionalized, scribed regions on single Si surfaces of a) the homologous series of 1-alkenes from 1-pentene to 1-octadecene, b) a series of alcohols and, c) a series of mixed monolayers on scribed Si from two 1-alkenes or from a 1-alkene and an alcohol. The preparations were performed in the air without any special treatment or degassing of chemicals. The ability to create surfaces with different monolayer coatings in precisely controlled regions should prove technologically valuable, for example, in creating functionalized surfaces to perform multiple bioassays.

[1] T. L. Niederhauser, G. Jiang, Y.-Y. Lua, M. J. Dorff, A. T. Woolley, M. C. Asplund, D. A. Berges, M. R. Linford, Langmuir 2001, 19, 5889-5900.

[2] T. L. Niederhauser, Y.-Y. Lua, Y. Sun, G. Jiang, G. S. Strossman, P. Pianetta, M. R. Linford, Chem.Mater. 2002, 14, 27-29. .

9:20am **AS-ThM4 Surface Analytical Characterization of SiO_2 Gradient Membrane Coatings on Gas Sensor Microarrays**, ***M. Bruns***, Forschungszentrum Karlsruhe GmbH, Germany, *H. Baumann,* Universität Frankfurt/Main, Germany, *M. Frietsch, E. Nold, V. Trouillet,* Forschungszentrum Karlsruhe GmbH, Germany, *R. White, A. Wright,* Thermo V.G. Scientific, England

The growing demand for inexpensive, space-saving and intelligent gas sensor systems led to the development of a gas sensor microarray at the Forschungszentrum Karlsruhe. The microarray currently comprises 38 sensor elements on an area of $4x8mm^2$ and is based on an 150 nm thick SnO_2 layer, the electrical conductivity of which is highly sensitive to the composition of the ambient atmosphere. The basic structure of the microarray is manufactured by R.F. magnetron sputtering, applying a shadow masking technique. Parallel platinum strip electrodes for the conductivity measurement are sputtered on top of the metal oxide, thus subdividing the latter into the initially identical sensor elements. In order to modify the gas response of individual sensor segments, a gas-permeable SiO_2 membrane with a thickness variation of approximately 2 to 50 nm was deposited across microarray using ion beam assisted deposition.[1] Auger electron spectroscopy already has been proven to be a powerful tool in quality control of the fabrication of gas sensor microarrays[2] and, therefore, was used for rapid evaluation of the geometrical integrity of the electrode pattern. The chemical state determination of the layer constituents was carried out by X-ray photoelectron spectroscopy. Parallel ARXPS (angle resolved XPS) data collected with the Thermo VG Theta Probe can provide thickness information from the SiO_2 membrane in a non-destructive manner using a well-controlled analysis area (X-ray spot size 50 µm). In addition, ellipsometry, nuclear resonant reaction analysis, and non-Rutherford backscattering spectrometry were used to achieve a comprehensive characterization.

[1] M. Frietsch, L.T. Dimitrakopoulos T. Schneider, J. Goschnick, Surf. Coat. Technol., 120-121 (1999) 265

[2] R. Schlesinger, M. Bruns, Thin Solid Films, 366 (2000) 265.

9:40am **AS-ThM5 Surface Properties of Chemically Processed Niobium**, ***E.S. Gillman***, *A.M. Valente*, Jefferson Lab

Many high-performance accelerators, such as CEBAF at Jefferson Lab, rely on superconducting radio-frequency (SRF) technology. SRF technology at Jefferson Lab is based on the use of superconducting niobium accelerating cavities. The accelerating cavities are contained in cryomodules where liquid helium maintains the temperature at 2 K. To realize the highest energy and lowest heat loss from these accelerators means improving the performance of the accelerating cavities. We have studied the surface of chemically processed, heat-treated niobium used in these cavities with angle-resolved x-ray photoelectron spectroscopy (ARXPS) to ascertain the effect of process conditions on cavity performance. Our data indicates correlations between the passivation oxide layer thickness and stochiometry with processing conditions and that processing conditions can be directly correlated with cavity performance. This work was supported by U.S. DOE Contract No. DE-AC05-84-ER40150, the Commonwealth of Virginia and the Laser Processing Consortium.

10:00am **AS-ThM6 DC Field Emission Analysis of GaAs and Plasma-source Ion Implanted Stainless Steel**, ***C. Hernandez***, *T. Wang, T. Siggins, H.F. Dylla,* Jefferson Lab, *N.D. Theodore, D.M. Manos*, College of William and Mary, *C.E. Reece*, Jefferson Lab

Field emission studies have been performed on a GaAs wafer and a sample of its stainless steel (SS) support electrode that are part of the new photocathode gun for the 10 kW upgrade FEL at Jefferson Lab. The objective of the studies presented here is to characterize the effect of both, the cleanliness of the wafer and the plasma source ion implanted layer on the electrode to suppress field emission. Field emission is the limiting factor to achieve the required 6 MV/m at the surface of the wafer. Potential field emitters are first located on the surface of 1-inch diameter samples with a DC field emission scanning apparatus at 60 MV/m, then each emitter is characterized by SEM equipped with EDS. The GaAs wafer was hydrogen cleaned before the study. The results show three emitters caused by indium contamination during wafer handling. The GaAs wafer thus shows good high voltage characteristics and the need to maintain cleanliness during handling. The SS sample is hand polished with diamond paste to a 1-micron surface finish, then implanted with N_2/SiO_2 in a plasma source ion implantation chamber in preparation for the field emission studies.[1]

[1] This work is supported by the US Dept. of Energy and the Office of Naval Research.

10:20am **AS-ThM7 Study on Electron Emission from Some Metals and Carbon Materials and the Surface Characterization**, ***S. Kato***, KEK & The Graduate University for Advanced Studies, Japan, *M. Nishiwaki*, The Graduate University for Advanced Studies, Japan

We focus on secondary electron emission from metals and carbon materials in conjunction with potential and actual problems of photoelectron instability and electron multipactering in several particle accelerators in the world. Therefore it is quite important to explore promising materials which have secondary electron yields as low as possible. While a plenty of reports on investigation of secondary electron emission was made over years, the experimental conditions with poor vacuum have deteriorated the quality of the data and lack of surface characterization has made understanding the data and applying the data to surface engineering confusedly difficult. For this purpose, an UHV system was newly developed which consisted of a x-ray source, an ultraviolet photon source, an electron gun, an ion gun, residual gas analyzers, a hemispherical energy analyzer and a sample manipulator with cooling and heating capabilities. This system gives us useful basic informations about dependences of secondary electron yields and the energy distributions on primary electron energy, material, the material temperature and the surface state. In-situ surface characterization of the materials was also performed before and after conditionings such as heating, gas exposure and electron or ion bombardments. Prepared materials were oxygen free copper (single and poly-crystalline), pure titanium, stainless steel, isotropic graphite and carbon fiber reinforced carbon composite. Mechanical surface roughing on the materials was attempted to reduce electron emission in addition. The introduction of the system, the measured results and the discussion will be described in this paper.

10:40am **AS-ThM8 Investigation of the Interfacial Interactions Associated with the Application of a Polymer Coating onto Oxide-free Phosphate Films on Metals**, ***Y.Q. Wang***, *P.M.A. Sherwood*, Kansas State University

This paper will report the results of a continuing study focused on preparing novel surface chemistries with oxide-free phosphate films on metal surfaces. We have developed a new more easily applied process, based on our earlier studies and patent for oxide-free phosphate films. The new process is carried out under ambient conditions using aqueous phosphoric acid. The chemistry of the surface prepared by the new process and its effects on the coating of polymers on metalic aluminum and iron will be investigated by XPS to evaluate the potential of this film to serve as a corrosion inhibitor and other applications. It will also be seen that the valance band photoemission, interpreted by band structure and other calculations can be used to study the interfaces involved in, is a very effective tool for conclusively identifying the surface species present.

This materials was based upon work supported by the National Science Foundation under Grant No. CHE-0137502.

11:00am **AS-ThM9 Valence Band X-ray Photoelectron Spectroscopy Studies of Different Forms of Sodium Phosphate**, ***A.L. Asunskis***, *P.M.A. Sherwood*, Kansas State University

Valence band X-ray photoemission can be used to identify subtle differences in surface chemistry. There are a very large number of phosphate species, and it is often important to distinguish between these species. Our group has been examining phosphate surfaces on metals, and has shown[1] that it is possible to prepare oxide-free phosphate films on the surfaces of a variety of metals (e.g. iron, aluminum, copper, and titanium) by treatment of the oxide-free metal surface with orthophosphoric acid. Studies of core X-ray photoelectron spectroscopy (XPS) are of little value in distinguishing between different phosphate species. We have shown that it is possible to distinguish between orthophosphate and metaphosphate from differences in the valence band region which can be understood by comparison with spectra predicted by band structure calculations. In this presentation we report the extension of our earlier studies to include linear phosphates of different chain length and other phosphate species. The spectra show that valence band XPS can be used to distinguish between these species and that the spectral differences can be interpreted by spectra predicted by band structure calculations. This material was based upon work supported by the National Science Foundation under grant No. CHE-0137502.

[1] J.A. Rotole and P.M.A. Sherwood, Chem. Mater., 13, 3933-3942 (2001).

11:20am **AS-ThM10 The Study of Vanadium Phosphates by Valence Band X-ray Photoelectron Spectroscopy**, ***D.J. Asunskis***, *P.M.A. Sherwood*, Kansas State University

This paper presents a study of various vanadium phosphates synthesized by the reaction of vanadium with phosphoric acid in a variety of conditions, including choice of solvent and acid hydration. It is known that the differences in the nature of the vanadium phosphates can impact their role in catalysis, and we are interested in the nature of vanadium phosphate films on metals. In this study valence band X-ray photoelectron spectroscopy, in conjunction with core level X-ray photoelectron spectroscopy, is used for the identification of the synthesized compounds. The valence band spectra, which have been interpreted by band structure calculations, prove to be a conclusive way to identify the species present in each of these compounds. This material is based upon the work supported by the National Science Foundation under grant No. CHE-0137502.

11:40am **AS-ThM11 Sorbed Water, as the Source of the Dissolved H_2 and D_2 In Metals at Friction**, *E.A. Rodina*, ***E.A. Deulin***, Bauman Moscow State Technical University, Russia

Results shows, that concentration of the H_2 dissolved in the steel 304 after keeping in normal atmosphere (pressure of H_2 P_{H2} =5*10^{-2} Pa, pressure of D_2 P_{D2}=7*10^{-6} Pa) is C_{H2} = 2*1019 at/sm^3, instead of theoretically expected C_{H2} = 2*10^{19} at/sm^3, similarly, for D_2, dissolved at P_{D2} = 7*10^{-6} Pa, its concentration, instead of theoretically expected $C^{theor}{}_{H2}$ = 8*10^{15} at/sm^3 is C_{D2} = 1*10^{18} at/sm^3. As for H_2 also as for D_2 it is possible to explain their increased concentration by the relay dissociation of sorbed water.[3] The results show that the residual atmosphere of H_2 or D_2 influences on ions exchange processes of D_2 and H_2 in layers of sorbed water. So, in the submitted results it is enough 0,002% dissociation of sorbed water to ensure the pointed mentioned concentration. Concentration of the dissolved gases (N=6000 cycles, Sigma= 1500 MPa, n = 600 cont/s) grows up to $C^{max}{}_{D2}$ = 2*10^{21} at/sm^3 and $C^{max}{}_{D2}$ = 3*10^{19} at/sm^3 as a result of mechanical action influence that corresponds to the 8,5% dissociation of H_2O, and corresponds to 0,1% dissociation of HDO (for used in a result of D_2 interaction from a surface).

[1] E.A. Deulin, A.A. Gatsenko, B.A. Loginov. Friction force of smooth surface of SiO2-Si02 as a function of residual pressure. Surface Science 433-435 (1999) 288-292.

[2] E. A. Deulin, R.A. Nevshupa. Deuterium penetration into the bulk of a steel ball of a ball bearing due to its rotation in vacuum. Applied Surface Science 144-145 (1999) 283-286.

[3] K.Akagi, M. Tsukada. Theoretical study of hydrogen relay dissociation of water molecules on Si(001) surfaces. Surface Science 438 (1999) 9-17.

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

Practical Surface Science II
Moderator: B. Beard, Akzo Nobel Chemicals, Inc.

2:00pm **AS-ThA1 Transferring Classical UHV Techniques into Ambient Pressure - Is the Gap Bridged for Electrons?**, ***A. Vollmer***, University of Cambridge, UK, *J.D. Lipp, G.E. Derbyshire,* Rutherford Appleton Laboratories, UK, *H. Weiss,* Universität Magdeburg, Germany, *D. Herein,* ACA, Berlin, Germany, *T. Rayment,* University of Cambridge, UK

Most traditional surface science methods are restricted to studies of model systems under 'ideal' conditions, most prominently single crystals in ultra-high vacuum (UHV). The interest in the development of surface science methods for investigations of systems with a more immediate, practical relevance (e.g., heterogeneous catalysts) remains strong, especially with a view to the difficulties in delineating relationships between interfacial behaviour under conventional "surface science" and "practical" conditions, i.e. high pressure environments. In the field of heterogeneous catalysis the terms "pressure gap" and "material gap" have been coined to describe the relationship between surface science and practical catalysis. Under UHV conditions, gas-surface-interactions are widely studied by means of electron detection (LEED, UPS, XPS, XAS and many more) while in gaseous environments electrons are strongly scattered and quickly attenuated. Until recently,[1] an efficient mode for energy-selective electron detection at ambient pressure was not available. We have now explored the possibilities of gas microstrip detectors (GMSD) as a promising tool for bridging the pressure gap between surface science and 'real world' conditions. We will show that energy-selective electron detection and depth profiling is possible for various systems operating under practical pressure conditions, including powders, layered structures, metals as well as insulators. Investigated systems include partial oxidation catalysts based on Vanadium oxides and phosphates. We will also report upon an ambient pressure surface sensitive scanning X-ray microprobe working under reaction conditions.

[1] T. Rayment et al, Rev. Sci. Instrum. 71 (2000) 3640.

2:20pm **AS-ThA2 Plan to Maximise Information Retrieval from the XPS Survey Scan**, ***J.E. Castle***, The University of Surrey, UK

The work to be described concerns the implementation of procedures designed to extract the maximum information possible from the initial survey scan typically made at the outset of XPS analysis of an unknown surface. The procedures resulted from detailed expert discussion of the issues at the recent 'IUVSTA Workshop No.34'. The procedures devised are intended to give guidance for those developing data systems having a degree of inbuilt inferencing capability. Here we have assessed the recommended procedures using off-line processing where necessary but have, as far as currently possible, mimicked the operation of a hands-off system. We will show in this paper the extent to which information retrieval can be enhanced and discuss the possibilities for this to be implemented in future datasystems.

2:40pm **AS-ThA3 Real World Surface Analysis**, ***W.R. Nieveen***, *T.F. Fister, P. Lindley*, Charles Evans & Associates - Evans Analytical Group **INVITED**

In todays short R&D-to-product cycle, there is often an oversimplification of the use and valuation of surface analysis. The dividing line is usually chosen between academic/institutional versus industrial or production environments and the most common divider is typically time. Both arenas are equally "real", but the utilization of equipment and instrumentation is typically quite dissimilar. Consequently, methodology between the two divisions is also substantially different. The outcome of any particular surface analytical experiment may have different significance depending on the environment in which it is conducted. The process by which decisions within the analysis are determined and the resulting decisions from the experiment's conclusion can greatly affect the way a particular analysis is performed. These intangibles frequently affect the perceived success or value of surface analysis. In this talk, we will look at the differences in methodology between typical industrial or production situations compared to the R&D or academic use of surface analysis. We will contrast the deadlines, purpose, and goals of typical R&D projects with the demands, timelines, and expectations of a production problem. We will examine the role of the analyst and the affect his/her experience within and outside the framework of surface analysis has on the results. Current real world examples (from both types of environments) using multiple technique surface analysis will be presented to illustrate the processes. Time permitting, examples of surface analytical methods as a research technique for materials characterization, a method for problem solving and/or failure analysis, and a metrology and/or QA/QC tool will be given. The incorporation of these different environments, the analytical decision processes, and the utilization of the results will be important for "expert system" development in surface analysis.

3:20pm **AS-ThA5 Nanoscale Tomography with the Focused Ion Beam**, ***R. Hull***, University of Virginia **INVITED**

We describe the use of focused ion beam sputtering to create tomographic reconstructions of objects at length scales ranging from tens of nanometers to tens of microns. This is achieved by imaging (with secondary electrons or secondary ion mass spectroscopy, SIMS) the sputtered surface at different depths in the sample. Computer interpolation of successive images then enables reconstruction of the 3D structure and chemistry. The final reconstructions typically contain several million independent voxels of data. We will describe experimental strategies for optimizing the realizable spatial resolution, for example by minimizing generation of topography arising from differential sputtering rates. We will also describe implementation of computer algorithms for interpolating between experimental images. The simplest algorithms employ linear interpolation of pixel intensities between successive images, but these techniques work well only where structures are relatively uniform along the normal to the sputtered surface. For structures with high curvature along the sputtering direction, we employ shape-based interpolation techniques (as developed for the medical tomography field) that enable complex geometrical forms to be reconstructed. Spatial resolution is defined primarily by the probe size and the lateral spread of the incident Ga ions in the sample for lateral resolution, and the implant depth for incident Ga ions and escape depth for secondary electrons/ions for vertical resolution. We have confirmed predicted resolution of order 20-30 nm by direct lateral and vertical detection of 22 nm layers in InAlP/InGaP heterostructures. Chemical sensitivities are greatly limited by the low ionization efficiency of most materials by primary Ga ions. Accordingly, we are exploring photon-based techniques for post-sample ionization of sputtered neutrals. This work is done in collaboration with A. Kubis and G. Shiflet (UVa), D. Dunn (IBM) and D. Backman (GE).

4:00pm **AS-ThA7 Electromigration Behavior of Single Crystal Copper**, *C.M. Contino, S.M. Schwarz,* ***L.A. Giannuzzi***, University of Central Florida

A preliminary report on the electromigration behavior of single crystal copper will be presented. A focused ion beam instrument was used to prepare single crystal copper samples oriented along [100] and [110]. Electromigration results of the single crystal samples indicate that the [100] oriented sample had better electromigration properties than the [110] oriented sample.

4:20pm **AS-ThA8 XPS Analysis under External DC and AC Bias**, ***S. Suzer***, *B. Ulgut*, Bilkent University, Turkey

Charging is a nuisance in XPS analysis and is usually circumvented by flooding the sample with low energy electrons. External biasing is an easier/cheaper alternative and can even give additional static or dynamical information about charging which can in turn be related to composition of the sample. In this contribution, we will present XPS spectra of Au/SiO2/Si system under various DC and AC (square-wave) bias conditions and discuss the issues related to charging and/or composition.

Applied Surface Science
Room: C-106 - Session AS+MM+BI-FrM

BioMEMS and Medical Devices
Moderator: K. Healy, University of California, Berkeley

8:20am **AS+MM+BI-FrM1 Characterization of Implant Surfaces**, ***M. Grunze***, University of Heidelberg, Germany **INVITED**

In this talk I will describe my personal recollection of the development of polymer coating (Polyzene FÂ®) for cardiovascular stents from concept to market. The idea was to develop a "stealth" surface coating for metallic stents which reduces inflammation, thrombosis and restenosis of the blood vessels. My talk discusses the design strategies of the polymer, development of the coating process and the necessary Surface Science characterization, protein, cell and bacteria adhesion experiments, the technical certification process, in vivo experiments in animal models, and the problems and successes in starting a new company to market the product. At this time the story is open-ended, since the results of ongoing long term clinical studies were not available at the time this abstract was written.

9:00am **AS+MM+BI-FrM3 Probing the Orientation of Surface-Immobilized IgG by ToF-SIMS**, ***H. Wang***, *D.G. Castner, B.D. Ratner, S. Jiang*, University of Washington

The orientation of a surface-immobilized IgG is crucial for its ability to detect antigen in biosensors. To probe the orientation of a surface-immobilized IgG, two factors are important. One is a powerful surface analysis technique while the other is a well-controlled surface for specific protein orientation. Static time-of-flight secondary ion mass spectrometry (ToF-SIMS) is well suited for this purpose since the sampling depth of ToF-SIMS (1-1.5 nm) is less than the typical dimension of most proteins (4-10 nm). At the same time, IgG orientation can be controlled by appropriately adjusting microenvironments (e.g., surface charges and solution properties). In this work, we apply ToF-SIMS combined with principle components analysis (PCA) to study the orientation of anti-hCG (human chorionic gonadotropin) on two controlled surfaces using its Fab and Fc fragments as references. The controlled surfaces are achieved using self-assembled monolayers (SAMs) with different terminal groups. Results show that the combined ToF-SIMS and PCA technique is able to probe the difference in orientations for ani-hCG adsorbed on different surfaces. In addition, ToF-SIMS results are compared with those from the protein structure. Consistency of these results indicates the reliability of this method.

9:20am **AS+MM+BI-FrM4 TOF-SIMS Analysis to Monitor Coating Processes in Organic and Biological Surfaces**, ***R. Chatterjee***, *B. Lakshmi, M.J. Pellerite*, 3M

Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) has proved to be very useful in molecular surface characterization of organic coatings, polymeric systems and biological surfaces. This paper will focus on the application of TOF-SIMS in identifying reaction processes involved in formation of bio-reactive surfaces and organic coatings. In SIMS, absolute quantitative analysis becomes difficult because the ion yield is highly dependent on the morphology and the physical and chemical nature of the surface. Different examples will be used to illustrate how with the use of suitable control experiments, relative quantitative analysis can provide direction in the development of surface modification and surface coating processes. Relative quantitation of TOF-SIMS data was applied to monitor the reaction of aminoacids to different bioreactive surfaces. TOF-SIMS was used to identify presence of different proteins in a multistep sandwich assay. In thin organic coatings, the degree of cure of the silane end group was correlated to the coating durability. Relative quantitation was applied to determine the degree of cure, specify process conditions needed for suitable curing, identify a suitable catalyst to reduce curing times and determine whether lack of cure is the cause of failure. The rate of cure of mono-, bis- and trifunctional silanes, and their effect on the coating durability was investigated.

9:40am **AS+MM+BI-FrM5 Characterization of Protein Interactions with MEMS Devices under Non-Static Conditions**, ***K. Lenghaus***, *J. Dale, D. Henry, J. Hickman,* Clemson University, *J. Jenkins, S. Sundaram*, CFD Research Corporation

The emerging field of micro electromechanical systems (MEMS), when directed to biological applications (environmental monitoring, biosensors etc.), requires an understanding of protein/surface interactions under conditions of flow at low concentrations. Previous protein studies have focussed on adsorption under static conditions and at high concentrations, which can not necessarily be extrapolated to those conditions found in Bio-MEMS under non-static or flow conditions. In an analogous system, the adsorption of proteins to surfaces in in vivo biological systems differs from other adsorption phenomena in that its consequences can be aggressively non-linear, with a biological system's response to minute deviations and changes greatly out of proportion to the magnitude of the change. Thus a relatively small fraction of aggressive sites can induce a response quite out of proportion to their numbers. To study both phenomena we have developed assays to allow enzymes to be quantified at ng/mL levels, and combined with a syringe pump we have created a simple, yet sensitive and robust test bed for protein adsorption under flow conditions. Using this approach, a PEEK capillary was found to have a small number of highly aggressive sites for protein adsorption, corresponding to 5% total surface coverage. These would serve as nucleation sites for further interactions in MEMS devices, and be difficult to detect by other methods. It was further shown that the adsorbed enzymes were in an active state, and this was used to confirm that the rate of desorption from the surface was of the order of 10-4.s-1, corresponding well with values derived from fitting the adsorption isotherm to a computational fluid dynamics model. Thus, studying enzyme adsorption can be used to give several useful insights into the adsorption/desorption behaviour of surfaces at low bulk concentrations of protein as well as generate insights for an in vivo system's protein nucleation behaviour.

10:00am **AS+MM+BI-FrM6 Selective Thermal Patterning of Self-Assembled DNA Monolayers on MEMS-based Microheater Devices**, ***T.H. Huang***, National Institute of Standards and Technology, *N. Ku,* Montgomery Blair High School, *R.E. Cavicchi, M.J. Tarlov*, National Institute of Standards and Technology

We report the selective patterning of self-assembled thiolated DNA probes on gold-coated microheater devices using temperature. The goal of our investigation is to utilize the rapid heating and cooling capabilities of MEMS-based microheaters to prepare biosensing surfaces and to monitor reactions such as DNA hybridization, melting and polymerase chain reaction (PCR). In this study, the self-assembly of thiolated-DNA probes on gold microheater array (four element array) is used as the model system. Modified DNA probes (5' end with disulfide and 3' end with fluorescein) are selectively immobilized onto the gold surface in several steps. First, a passivating layer consists of 1-mercapto-6-hexanol (MCH) is self-assembled onto the gold microheaters. The temperature for one the four heaters is elevated to ca. 200 ^{o}C to drive off the MCH. Then the thiolated DNA probes are deposited onto the freshly exposed bare gold surface. Using this method, one can use temperature to selectively deposit different DNA probes on specific heaters. The presence of the DNA probes on the surface is detected using fluorescence microscopy. In order to use the DNA-microheater surface to monitor DNA melting reactions or PCR (which require cycling to high temperatures), it is important for the probe to be thermally stable at the operating temperatures (i.e. 85 ^{o}C). We will also present results on the thermal stability of thiolated DNA monolayers on gold.

10:20am **AS+MM+BI-FrM7 Soft and Fuzzy Polymer Coatings for Microfabricated Neural Prosthetic Devices**, ***D.C. Martin***, The University of Michigan, *X. Cui,* Unilever, *R. Kim, J. Yang, Y. Xiao*, The University of Michigan **INVITED**

Neural prosthetic devices facilitate the functional stimulation of and recording from the peripheral and central nervous systems. It is important that these implantable devices function in vivo for long periods of time. Bioactive and electrically conductive materials are deposited on the surfaces of neural microelectrode arrays through various means to build a stable interface for better biocompatibility and signal transduction. To mediate the mechanical property differences between the brain tissue and silicon device, integrate the device within tissue and minimize the host reaction, bioactive coatings were developed that can be applied over the whole surface of the silicon micro-devices. One approach that has been developed is electrospinning of protein polymers to form a porous film composed of electrospun nano-scale protein fibers with cell-binding sites exposed. Another ongoing approach has been to coat the device with bioactive hydrogel materials which change volume according to their environment, and therefore integrate the device in the tissue with minimal insertion damage. To stabilize the connection between neurons and the electrode sites and facilitate the signal transduction from electrically conductive metal electrode to the ionically conductive tissue, conductive polymers together with bioactive molecules were co-deposited on the electrode site areas by electrochemical deposition. The coatings presented a fuzzy and conductive surface which lowered the impedance of the electrode by 1 to 2 orders of magnitude. The bioactive molecules with cell binding ability in the deposited films on the electrode sites were shown to be able to anchor neurons in both in vitro and in vivo experiments.

11:00am **AS+MM+BI-FrM9 Voltage-Dependent Assembly of the Polysaccharide Chitosan onto an Electrode Surface**, *L.-Q. Wu, A.P. Gadre, H. Yi, M.J. Kastantin, G.W. Rubloff, W.E. Bentley, G.F. Payne,* ***R. Ghodssi***, University of Maryland

We examined the assembly of a basic polysaccharide - chitosan - from solution onto electrode surfaces as a result of voltage bias on the electrode. Chitosan is positively charged and water-soluble under mildly acidic conditions, and is uncharged and insoluble under basic conditions. We observed that chitosan is deposited from acidic solution onto the surface of a negative electrode and that the thickness of the deposited layer is dependent upon the deposition time, the applied voltage, and the chitosan concentration. No deposition occurs on the positive or neutral electrode. Once deposited and neutralized, the chitosan layer can be retained on the electrode surface without the need for an applied voltage. Infrared (FTIR) and electrospray mass spectrometry (ES-MS) confirmed that the deposited material was chitosan. The voltage-controlled deposition of chitosan provides a means for anchoring biopolymer material in specific locations in bioMEMS environments, such as encapsulated microfluidic devices fabricated in our laboratory using MEMS-based polymeric materials (EPON SU-8, Polypyrrole and Polydimethylsiloxane). Furthermore, chitosan's amine functionality should enable standard coupling chemistries to be exploited to anchor additional biomolecules (e.g. DNA and proteins) to the surface of bioMEMS devices.

11:20am **AS+MM+BI-FrM10 Alternative Approaches to Microfluidic Systems Design, Construction and Operation**, ***D.J. Beebe***, University of Wisconsin, Madison **INVITED**

Many approaches to the construction of microfluidic systems have appeared in the last few years including glass and silicon etching and bonding, laser machining, micromolding and others. Here we present an alternative approach to the design, construction and operation of microfluidic systems that we call Âµfluidic tectonics (ÂµFT) that compares to injection molding in cost, but allows for a wide variety of functionality. ÂµFluidic Tectonics utilizes liquid phase photopolymerization, responsive materials and in situ fabrication to achieve elegant yet functional designs. Ultra rapid microchannel fabrication (2 minutes) is demonstrated using off the shelf components (glass microscope slides, polycarbonate top, simple UV lamps and transparency masks). The process eliminates the need for traditional bonding to achieve a closed channel and no master is required (as in elastomeric micromolding). The same basic process has been used to create filtering, flow control, readout (chemical and biological) and mixing components. Thus, the construction platform leads to highly integrated systems by using a single fabrication process and class of materials (photopolymerizable polymers). Closed loop feedback control is demonstrated without the use of electronics. A single structure created in situ from responsive materials performs the sensing and actuation functions. The responsive component senses the local chemical environment and undergoes a volume change in response to changes in the local environment. The volume change is coupled to a valve that regulates the compensating stream providing closed loop regulation. The design flexibility ÂµFT combined with the ease of fabrication and low cost (similar to injection molding) enhances the microfluidic toolbox and broadens the base of potential designers and users by simplifying the construction process and reducing the infrastructure needed to create and use microfluidic systems.

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