

Monday Morning, November 13, 2006

Applied Surface Science

Room 2005 - Session AS+BI+NS+NM-MoM

Organic Surface Modification and Nanoscale Chemical Patterning

Moderator: R. Haasch, University of Illinois, Urbana

8:00am AS+BI+NS+NM-MoM1 Biomolecular Lithography on GaAs Surfaces, A. Ivanisevic, Purdue University INVITED

Atomic force microscopy (AFM) was used to fabricate well-defined peptide templates onto GaAs surfaces via Dip-Pen Nanolithography (DPN). DPN is a powerful technique to write specific organic and/or inorganic molecules onto a surface with an AFM tip. In this work, DPN was used to construct arrays of peptides with nanometer features. TAT peptides (e.g. CGISYGRKKRRQRRR) which exhibit rapid uptake in cells, were patterned onto the surface in either contact or tapping mode. Several techniques were used for the characterization of the modified surfaces: X-ray photoelectron spectroscopy (XPS), Fourier Transforms Infrared (FT-IR) spectroscopy and contact angle. Transmission FT-IR provided structural information such as peptide conformation. The complementary analysis confirmed the binding of the peptide onto the substrates and allowed to quantify the density of immobilized peptides on a given surface. Furthermore, the nanoscopic features were successfully used in recognition experiments where an RNA sequence with a loop structure, known for its specific interaction with the peptide, was tested. The results in this report indicate that one can use nanolithographic strategies to pattern GaAs surfaces, and therefore provide a proof-of-concept experiment that can be transferred in complex microfabricated semiconductor architectures.

8:40am AS+BI+NS+NM-MoM3 The Effect of Ring Substitution Position on the Structural Conformation of Mercaptobenzoic Acid Self-Assembled Monolayers on Au(111), J.R.I. Lee, Lawrence Livermore National Laboratory; T.M. Willey, J. Nilsson, L.J. Terminello, J.J. De Yoreo, T. van Buuren, Lawrence Livermore National Laboratory

Mercaptobenzoic acid (MBA) is a viable alternative for preparing SAMs with carboxyl functionality. These molecules, as opposed to carboxyl-terminated alkanethiols, offer an extended pi-bonded system formed by the aryl and carboxyl groups facilitating charge transfer, and these extremely thin SAMs (< 8 Angstroms) have been shown via STM to contain a high degree of structural order. Furthermore, three different isomers of mercaptobenzoic acid may lead to differing surface properties. In this work, the orientation and bonding of self-assembled monolayers of the three positional isomers of mercaptobenzoic acid adsorbed on gold are investigated using near edge X-ray absorption fine structure (NEXAFS) spectroscopy and photoemission spectroscopy (PES). The isomer of MBA and solvent chosen in SAM preparation has considerable bearing upon film morphology. Monomers of 3- and 4-MBA assume an upright orientation on the Au substrates in monolayers prepared using an acetic acid in ethanol solvent. The aryl ring and carboxyl group of these molecules are tilted from the surface normal by a colatitudinal angle of ~ 30 degrees. Preparation of 4-MBA SAMs using pure ethanol solvent, a more traditional means of synthesis, had no appreciable effect upon the monomer orientation, but S(2p) PES measurements illustrate that it results in extensive bilayer formation via carboxyl group hydrogen-bonding between 4-MBA monomers. In 2-MBA monolayers prepared using acetic acid/ethanol solvent, the monomers adopt a more prostrate orientation on the Au substrates, in which the aryl ring and carboxyl group of the molecules are tilted ~ 50 degrees from the surface normal. This configuration is consistent with an interaction between both the mercaptan sulfur and carboxyl group of 2-MBA with the underlying substrate. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Science, and performed under the auspices of the U.S. DOE by LLNL under contract No. W-7405-ENG-48.

9:00am AS+BI+NS+NM-MoM4 XPS Analysis of Arenes and Proteins on Gold Substrates Attached by Electrochemical Reduction of Aryldiazonium Salts, J.L. Fenton, University of New Mexico; S.M. Dirk, D. Wheeler, Sandia National Labs; J.E. Fulghum, University of New Mexico

The properties of most materials can be altered by the attachment of molecules to their surface. Recent work has shown that diazonium salts can be used to attach aryl compounds to metal and semiconductor surfaces including silver, iron, platinum, silicon, and glassy carbon. Diazonium salts can be electrochemically reduced in acetonitrile leading to the attachment of aryl groups to the surface of a substrate. The attachment of aryl compounds using diazonium salts developed in our work, allows one to

attach aryl compounds with different organic moieties onto metal substrates including gold. Aryl organic layers can be made of different thicknesses, and stacked structures can be created by alternating layers of molecules. This work is then expanded upon to attach proteins to metal surfaces. This approach provides a methodology to generate arrayed proteins on electrode arrays without the use of microfluidic methods such as ink jetting etc. The development of protein arrays can often provide high-throughput, quantitative measurement of receptor-ligand complexation giving an understanding of protein function, modification, and regulation. X-ray photoelectron spectroscopy (XPS) is used to deduce the different types of chemistries in single molecule samples, stacked structures, and surface tethered proteins. Angle resolved XPS is used to determine the relative location of each molecule in the stacked structures and possible orientation of proteins as well as to deduce the existence of azo linkages.

9:20am AS+BI+NS+NM-MoM5 Challenges in the Modification and Characterization of Two- and Three-Dimensional Biointerfaces, M. Textor, ETH Zurich, Switzerland INVITED

Surface modifications based on biochemical or biological principles are important tools for the fabrication of biosensor chips, biomedical devices such as implants, and of drug delivery carriers. Moreover, well-designed model biointerfaces have substantially contributed in the last decade to a better insight into fundamental aspects of cell-surface interaction. An overview will be given on tools enabling the surface engineer to tailor the interface of biomaterials, with special emphasis on the approach of eliminating non-specific adsorption and adding to such a silent surface biological functionalities. Preservation of active conformation and optimum presentation (orientation, density) of surface-immobilized moieties are particular challenges in this field. Different approaches to micro- and nanopatterning of surfaces, their specific advantages/disadvantages and applications in biorelated fields are discussed. Special emphasis is placed on methods that combine top-down (e.g., lithography) and bottom-up (self-assembly) approaches. Substantial new insight into the factors that govern cell-surface interactions and cell differentiation has recently been gained by using two-dimensional (2D) patterns. There is, however, an increasing interest to explore (stem) cell development in 3D microwells with well-controlled geometry (shape/size), surface chemistry and mechanical properties (substrate stiffness). The challenges of independently tailoring chemistry and structure/topography are addressed; self-assembly techniques are in this respect particularly useful. Finally, characterization/imaging techniques that allow the monitoring of biointerface reactions in situ, in real time and quantitatively are important tools; selected methods will be presented based on highly surface- and detection-sensitive evanescent-field-based sensing.

10:20am AS+BI+NS+NM-MoM8 Nanoscale Chemical Patterning and Architectures, P.F. Nealey, University of Wisconsin INVITED

Diblock copolymers are self-assembling materials consisting of two polymer chains connected at one end that tend to form ordered nanostructures, including spheres, cylinders, and lamellae, whose shape and dimensions depend on the molecular weight and composition of the polymer. Block copolymer lithography refers to the use of these ordered structures in the form of thin films as templates for patterning through selective etching or deposition. Already block copolymer lithography has been used to pattern dense periodic arrays for the applications such as quantum dots, nanowires, magnetic storage media, increased capacitance gate devices and FLASH memory. One of the current goals in block copolymer nanolithography is to reproduce many of the characteristics of the lithographic process used ubiquitously in nanomanufacturing, including pattern perfection over macroscopic areas, the ability to pattern arbitrary and non-regular geometries, dimensional control of features within exacting tolerances and margins, and registration and overlay. Two strategies will be discussed to integrate self-assembling materials into existing manufacturing practices so as to achieve molecular-level process control and the ability to produce useful architectures: directed assembly of block copolymers on topographically patterned substrates, and directed assembly of block copolymers on chemically nanopatterned substrates.

11:00am AS+BI+NS+NM-MoM10 Tailoring of Functional Nano-Patterned Surfaces for Biosensing Applications by Combination of Plasma Processes and Electron-Beam Lithography, F. Brétagnol, L. Ceriotti, A. Valsesia, T. Sasaki, D. Gilliland, G. Ceccone, P. Colpo, F. Rossi, IRC-IHCP-BMS, Italy

Fabrication of micro and nano-patterned surfaces with a well defined geometry and a controlled chemistry is a fundamental step for the development of bioengineered materials. Micro-arranged surfaces

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containing functionalities such as cell or protein adhesive in a non non-adhesive matrix provide a very useful tool in a large field of applications (tissue engineering, cell behavior investigations , artificial growth of neurons networksâ?}). Numerous methods have been successfully developed for the production of such surfaces including conventional photolithography, photochemistry , micro-contact printing , micro fluidic patterning . Nevertheless, the development of surfaces chemically patterned at nano scale is still a challenging issue for the implementation of new generation of miniaturized biochips and for the study of cell surface interactions. In this study, we present an innovative method for the fabrication of chemically nano-patterned surfaces. Maskless lithography based on electron-beam technique was successfully combined with plasma-based processes to create COOH terminated spots over a PEO-like matrix. Spots from micron to submicron size have been created. Quality control of the patterned surface was studied by Atomic Force Microscopy, XPS and ToF-SIMS analysis. Experiments with fluorescent proteins on the patterned surfaces exhibit a preferential adhesion on the active region showing the ability of this technique for the design of biosensing platforms.

11:20am **AS+BI+NS+NM-MoM11 Optically-Stimulated Surface Diffusion Exploited for Directed Self-Assembly on Amorphous Semiconductors**, *E.G. Seebauer, Y. Kondratenko*, University of Illinois at Urbana-Champaign

Nanoscale device fabrication technologies require toolsets for miniaturization and organization of materials at nanometer dimensions. Current toolsets have developed from two diametrically opposite strategies: top-down and bottom-up. This laboratory is taking a different approach based on a new physical mechanism for photostimulated diffusion discovered here. This new strategy combines attractive features of top-down and bottom-up approaches by exploiting the self-organization capabilities latent in amorphous materials, but in a way that can be controlled by optical or electron beam exposure tools. We have developed a new surface self-assembly method at the 10-200 nm length scale using amorphous semiconducting materials. Patterned optical or electron beam exposure yields a spatially varying surface mass flux that, when performed at an annealing temperature just at the cusp of crystallization, provides the extra nudge to crystallize subcritical nuclei in regions dictated by the light flux. The full-fledged crystallites then grow by surface diffusion and Ostwald ripening until the desired fraction of the film has accreted onto the original nuclei. We have demonstrated this technique with titanium dioxide as the substrate material. This scheme should apply to a wide variety of semiconducting materials on nearly arbitrary substrates to form nanoarrays, nanowalls, and possibly three-dimensional structures. Possible applications include chalcogenide semiconductors for data storage media; nanoparticles arrays for direct use in sensors and solar cells; and semiconductor arrays for indirect use as seed layers for the subsequent deposition of sintered particle films in fabricating advanced ceramics and devices such as rechargeable batteries, solar cells, gas sensors, and photonic band gap materials in solar windowpanes.

11:40am **AS+BI+NS+NM-MoM12 Nanowires and Nanodevices via Assembly of Clusters**, *S.A. Brown*, Nano Cluster Devices Ltd, New Zealand

We report the achievement of contacted electronic devices, self-assembled from atomic nanoclusters. Features of this technology, which overcomes the difficulties in the assembly of building blocks inherent to many bottom-up approaches to nanotechnology, include: Interchangeable cluster sources so as to have available a wide variety of cluster materials in a useful size range, allowing exploitation of novel structures and properties. Self-assembly methods which avoid time consuming positioning of building blocks. Use of lithographic processes which are compatible with both cluster deposition technology and standard microelectronics fabrication protocols. Understanding of basic physical assembly processes in order to predict and control device formation, including availability of suitable computer simulations. In this paper we will review the assembly methods developed, which include directed assembly in silicon V-grooves and on polymer-patterned surfaces, as well as stencilling techniques. We will then focus on the application of these techniques to one class of devices which have been realised i.e. cluster-assembled hydrogen sensors. These sensors are realised by the deposition of Pd clusters on a substrate such that one or several conduction paths are formed between a pair of contacts. The sensing principle relies on the expansion of Pd clusters and the resulting change of conductance as a result of their absorption of hydrogen and we have demonstrated very high sensitivities.

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Room 2005 - Session AS-MoA

Developing Methods for Data Analysis

Moderator: S. Pachuta, 3M

2:00pm **AS-MoA1 Molecular Structure - G-SIMS with SMILES**, *I.S. Gilmore, F.M. Green, M.P. Seah*, National Physical Laboratory, UK

G-SIMS is a powerful method for the identification of organics and complex molecules at surfaces. For complex molecules, evaluating the molecular structure can be key to correct identification. We have shown that the molecular structure may be reassembled from fragment ions by studying the evolution of G-SIMS intensities as the surface plasma, with effective temperature $T_{\text{sub p}}$, is varied, known as G-SIMS-FPM. Here, we develop a novel approach based on SMILES (Simplified Molecular Input Line Entry Specification), to assist the reassembly process through evaluation of the fragmentation pathways of given molecular structures. The SMILES molecular model format allows the molecular structure to be expressed in a logical computer readable way. A computer program has been developed that takes a parent structure and goes through every possible fragmentation providing a tree-structure of fragmentation products. This fragmentation map thus comprises all the possible products without considering relative intensities. For any fragment it is then possible to identify the molecular structure, the mass and the pathway to the parent. By applying this process to many types of parent molecule a foundation library of fragments and pathways is developed. Using G-SIMS-FPM some of these pathways for the unknown molecule can be mapped out. Not all pathways are mapped because some of the fragmentation cascades may be weak and some may only occur for the neutral molecules that are not observed by SIMS. We find that there is a good correlation with peaks in G-SIMS-FPM and the fragmentation maps generated using this approach. The SMILES-based fragmentation maps provide significant help in identifying the molecular structure and this will be illustrated with different complex molecules. @FootnoteText@ @footnote 1@ I. S. Gilmore and M. P. Seah, Appl. Surf. Sci., 231-232 (2004) 224. @footnote 2@ I. S. Gilmore, F. M. Green and M. P. Seah, Appl. Surf. Sci., In the press.

2:20pm **AS-MoA2 Strategies for ToF-SIMS Data Complexity Reduction: A Comparison of G-SIMS and Multivariate Analysis Applied to PLGA Biopolymer Systems**, *F.J.M. Rutten, R. Ogaki*, The University of Nottingham, UK; *S. Li, M. Vert*, University of Montpellier, France; *M.R. Alexander*, The University of Nottingham, UK; *I.S. Gilmore*, National Physical Laboratory, UK; *M.C. Davies*, The University of Nottingham, UK

Amongst the plethora of surface analytical techniques currently available static (time-of-flight) secondary ion mass spectrometry (SIMS) stands out as a very powerful technique capable of yielding highly specific chemical information with often exquisite sensitivity. Information of this kind is more often than not crucial to understand highly complex biomaterial interfaces, such as surface interactions with cells and proteins in anti-fouling or tissue engineering applications. In this paper we present a comparative study of two SIMS spectral analysis approaches applied to a range of copolymers consisting of varying amounts of lactic and glycolic acid. Poly(Lactic-co-glycolic acid) (PLGA) is biodegradable and as such currently in use in a number of applications in the biomaterials field, such as tissue engineering scaffolds and drug delivery systems. A drawback of SIMS relates to the rather violent process involved in the generation of diagnostic secondary ions, which involves the impact of highly energetic ions leading to the formation of a range of charged fragments for a single molecular species. Whereas a wealth of information is captured in the resulting mass spectra, their complexity often precludes interpretation of all but the most prominent fragments. At present two approaches show great promise in reducing the complexity of SIMS spectra, thus maximising extractable information: Gentle-SIMS (G-SIMS) uses acquired data with different levels of fragmentation to extrapolate to lower surface plasma temperatures and hence amplifies otherwise weak but highly diagnostic larger mass fragments (e.g. Ref. 1). Multivariate analytical approaches reduce complexity by generating new variables which contain the most pertinent parts of spectra, with the possibility to relate this to surface chemistry. The relative merits of both techniques are discussed for PLGA-drug systems. @FootnoteText@ @footnote 1@ I.S. Gilmore, M.P. Seah, Appl. Surf. Sci. 231-232 (2004) 224 and refs. therein.

2:40pm **AS-MoA3 Multivariate Analysis of Correlated Spectral Images**, *J.A. Ohlhausen, M.R. Keenan, P.G. Kotula*, Sandia National Laboratories; *V.S. Smentkowski*, General Electric Global Research Center **INVITED**

Spectral imaging is a very powerful approach for collecting large amounts of potentially very useful data needed to characterize a material surface. The challenge arises with analyzing the large data sets in an unbiased way. This challenge can be overcome for single spectral images using multivariate statistical analysis (MSA) methods developed at Sandia. This presentation describes the application of MSA to the even greater challenge of correlated analyses. Specific examples that will be described include: Correlating positive-ion TOF-SIMS spectral images from multiple specimens comparing different process conditions; Correlating TOF-SIMS spectral images in the depth dimension to perform comprehensive 3D analysis; Correlating positive and negative TOF-SIMS spectral images from the same areas of a specimen; Correlating TOF-SIMS and electron-excited x-ray spectral images; and finally the correlation of XPS spectral images with Valence Band spectral images. Remaining challenges and pitfalls in correlated single- and multiple-technique spectral image analyses will also be discussed. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

3:20pm **AS-MoA5 X-ray Photoelectron Spectroscopy (XPS) Multi-Spectral Imaging of Aluminum Alloy Surfaces using Principle Component Analysis**, *C.H. Lee*, University of Manchester, UK, United Kingdom; *J. Walton, G.E. Thompson*, University of Manchester, UK; *M.R. Alexander*, University of Nottingham, UK

Aluminum alloys are of technological importance in most market sectors, ranging from architecture through aerospace to electronics products. Consequently, such alloys are the subject of much interest, particularly the near-surface and surface properties, which influence behaviour such as corrosion and adhesion of subsequent coatings. The aim of this study is to spatially resolve constituent particles in selected aluminium alloys and to disclose their contributions to the adsorption of a self-assembled flourinated alkyl phosphonic acid ($C_{10}F_{21}CO_2H$). Thus, XPS images have been obtained at small energy steps on both AA2024 T3 and AA6016 T4 aluminium alloys to maximize the acquired spectral information, which has been extracted using a multivariate statistical analysis approach (MVA) consisting of singular value decomposition (SVD) and principal component analysis (PCA). @footnote 1@ As a result, noise-reduced and background-corrected multispectral imaging has revealed the constituent second phase particles in the respective alloy systems, the particles distribution has been correlated with scanning electron microscope (SEM) and optical microscope images. Comparison of the surfaces before and after in-situ argon ion etching indicated preferential oxidation of aluminium formed with a copper enriched phase immediate beneath the oxide layer in the AA 2024 T3 aluminium alloy. As for, AA 6016 T4 aluminium alloy, the behaviour of Al-Fe-Si and Mg_2Si particles has been compared. The previous finding has been used to examine the chemisorption of flourinated alkyl phosphonic acid self-assembled layer onto the oxidised alloy systems. The multispectral XPS images show that the molecule assembled relatively uniformly on the 2024T3 compared to a heterogeneous distribution observed on the 6016T4. @FootnoteText@ @footnote 1@ J. Walton and N. Fairley J. Electron Spectrosc. Relat. Phenom. (2005) 148 29-40.

3:40pm **AS-MoA6 High Spatial Resolution XPS and AES Applied to the Understanding of Interfacial Delamination in Microelectronics**, *H. Piao, L. Le Tarte*, General Electric Co.; *N. Fairley*, Casa Software Ltd.

X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES) are the most widely used techniques for quantitative surface analysis. XPS is mainly dedicated to the identification of chemical composition/bonding on surfaces, while the high spatial resolution in AES has made it an established technique for determining the localized defects or other features distributed on surfaces. Although the spatial resolution in XPS has been much inferior to that in AES, the recent development of XPS instrumentation with near-micron spatial resolution has advanced the capability of elemental and chemical state imaging accompanied by small area analysis. @footnote 1@ The goal of this presentation is to show how the combined uses of XPS and AES at enhanced spatial resolution have significantly improved the understanding of interfacial delamination and related problems encountered in the production of electronic devices in the field of microelectronics. A few examples of the application of surface

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analysis for adhesion problems will be presented. In the presentation, the mathematical procedure using Principle Component Analysis (PCA) in the reduction of noise in XPS images² will also be described. The purpose of the PCA is to identify the abstract factor images containing significant information and reconstruct the images only using these factors without noise, therefore resulting in the set of images with enhanced signal-to-noise. The dramatic improvements in the image contrast and chemical component determination from multi-spectral image data sets will be demonstrated. ¹D. Briggs and J.T. Grant, *Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*, Surface Spectra/IMPublications, 2003.²N. Fairley and A. Carrick, *The Casa Cookbook*, Acolyte Science, 2005.

4:00pm AS-MoA7 Structure Elucidation of Nano-Composite Catalysts by Multivariate Analysis and Regression Modeling of XPS Data, K. Artyushkova, J.E. Fulghum, T.S. Olson, P. Atanassov, University of New Mexico

A new class of non-platinum electrocatalysts, based on pyrolysed porphyrins), was studied using X-ray photoelectron spectroscopy (XPS) in combination with multivariate analysis. Understanding the CoTMPP electrocatalyst structure in combination with surface medications occurring during pyrolysis requires identification of subtle changes in a very complex system. Deconvoluting numerous overlapping photoelectron peaks is a particular challenge in this case, as new species formed during pyrolysis may appear at the same binding energy as existing species. High-resolution spectra acquired from the precursor and electrocatalysts pyrolyzed at various experimental conditions were curve-fit using a) individual peaks of constrained width and shape as well as b) experimentally obtained photopeaks from the precursor and additional peaks required for a complete curve fit. Principal Component Analysis (PCA) was applied to quantitative results from the curve-fits of both types of spectra of pure elements, and various combinations, to identify types of species both formed and destroyed during the pyrolysis process and to find correlations between them. It was established that the catalyst presents a nano-composite of highly dispersed pyropolymer with remaining Nx-centers inserted in a graphite-like matrix. Approximately 50% of the metal is Co²⁺ associated with remaining N₄-centers. The remaining cobalt is present in crystallites of metallic Co, coated with thin layer of CoO. The distribution of these types of moieties is directly related to the efficiency of oxygen reduction. A Spectra-to-property relationship was developed by applying multivariate regression models correlating XPS data with rotating-ring disk electrode (RRDE) data for the CoTMPP catalyst treated in various acids which selectively remove chemical moieties. These models have a potential for predicting the chemical composition of the CoTMPP catalyst which optimizes electrochemical performance.

4:20pm AS-MoA8 Attenuation Lengths for Measurement of SiO₂ Film Thicknesses by XPS, C.J. Powell, National Institute of Standards and Technology; W.S.M. Werner, W. Smekal, Technical University of Vienna, Austria

Effective attenuation lengths (EALs) are needed for measurement of film thicknesses by XPS, and have often been obtained from the NIST Electron Effective-Attenuation-Length Database.¹ These EALs are derived from a model in which it is assumed that the substrate and the overlayer film have the same electron-scattering properties. We have used the new NIST Database for the Simulation of Electron Spectra for Surface Analysis (SESSA)² to compute EALs for thin films of SiO₂ on Si. With SESSA, the actual scattering properties for each material are utilized, and the resulting EALs are considered more reliable. EALs have been calculated for two emission angles and several film morphologies to simulate recent careful experiments:³ (a) an SiO₂ layer of variable thickness (1.4 nm to 7.6 nm) on Si; (b) an SiO₂ layer of variable thickness and three thin intermediate suboxides on Si; (c) a carbonaceous layer, an SiO₂ layer of variable thickness, and three intermediate suboxides on Si. The new EALs show a larger variation with SiO₂ thickness than found previously.⁴ The implications of these results for SiO₂ thickness metrology will be discussed. ¹<http://www.nist.gov/srd/nist82.htm> ²<http://www.nist.gov/srd/nist100.htm> ³M. P. Seah and S. J. Spencer, *Surf. Interface Anal.* 37, 731 (2005). ⁴C. J. Powell and A. Jablonski, *J. Vac. Sci. Tech. A* 19, 2604 (2001).

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Room 2005 - Session AS+SS-TuM

Environmental Materials and X-ray Spectroscopies

Moderator: D.J. Gaspar, PNNL

8:00am AS+SS-TuM1 Time-of-Flight SIMS in the Earth and Planetary Sciences, E.P. Vicenzi, D. Rost, Smithsonian Institution **INVITED**

Spatially-resolved chemical analysis of geological materials is typically performed by techniques that can best be described as near-surface methods, e.g. electron beam-induced X-ray microanalysis, or, laser ablation ICP-MS. A limited number of studies in recent years made use of legitimately surface sensitive techniques, such as Time-of-Flight Mass Spectrometry. The full mass spectrum imaging capability of ToF-SIMS has proved advantageous for extracting a high information content relative to the amount of sample consumed. The high information/sample mass ratios are particularly beneficial, even demanded in some cases, for the examination of extraterrestrial specimens. Over the past several years we have applied ToF-SIMS to the study of Martian meteorite specimens, particularly the alteration phases that formed in an aqueous environment at low temperatures. Through the analysis of these micrometer to submicrometer structures we have begun to address issues regarding the nature of fluid that flowed beneath the surface of Mars, as well as the number of fluid pulses that infiltrated rocks near the surface of the planet. Although no terrestrial analogues for the Martian meteorites are known, we will present results regarding the redistribution of the ultralight elements Li and B in similar Earth rocks by water-rich fluid alteration. NASA's highly successful STARDUST mission recently (January, 2006) returned the first samples of a comet to Earth, and is providing space science researchers with a first-hand look at some of the oldest material in the solar system. We anticipate receiving aliquots of Stardust from the curation facility at Johnson Space Center in mid 2006 and will report on our initial findings of this ultra-precious material.

8:40am AS+SS-TuM3 Characterization of Thin Films Produced by a Simulated Radioactive Dispersal Device, D.L. Blanchard, Jr., L.A. Snow, G.J. Lumetta, B.J. Cook, Pacific Northwest National Laboratory; F.T. Harper, Sandia National Laboratories

We have examined the surfaces of materials subjected to a simulated radioactive dispersal device (RDD), and find significant differences in the composition of the deposited surface films depending on the material and the distance from the blast. Coupons of aluminum, concrete, and other materials, roughly 1 cm square by 1 mm to 3 mm thick were placed at distances of 5, 10 and 25 feet from the center of the blast. The simulated RDD contained non-radioactive cesium (Cs) as a surrogate for radioactive Cs. X-ray Photoelectron Spectroscopy (XPS) reveals carbon films with incorporated Cs on the surface of the exposed materials. Depth profiling by ion sputtering shows that the thickness of the film, the character of the transition from carbon film to substrate material (abrupt or gradual), and the film composition vary greatly with distance from the blast and the material exposed.

9:00am AS+SS-TuM4 Characterization of Electrocoagulation Wastewater Treatment Floc and Aging Effects, J.A.G. Gomes, D.L. Cocke, H. Moreno, Lamar University; H.G. McWhinney, Prairie View A&M University; G.M. Irwin, E. Peterson, Lamar University

Analysis of contaminated water and the methods of water quality remediation, recycle and reuse are increasingly dependent on materials science. Metal poisoning in drinking water such as As has not only led to a health crises in third world countries such as Bangladesh and Mexico, but also threatens developed countries like the United States. Water dispersed materials containing iron or aluminum hydroxides /oxyhydroxide species can efficiently remove arsenic from water or wastewater. The detailed mechanisms of how this occurs are still being sought. Electrocoagulation (EC) is a very promising technique to produce such materials and remove arsenic and other heavy metals from aqueous media. In this paper, we discuss the characterization of these EC-flocs with and without metal pollutants using different analytical techniques, such as FT-IR, XRD, XPS, SEM/EDS and Mössbauer spectroscopy. Results reveal expected crystalline iron oxides (magnetite (Fe₃O₄), lepidocrocite (FeO(OH)), iron oxide (FeO)) and aluminum oxides (bayerite (Al(OH)₃), diaspore (AlO(OH)), mansfieldite (AlAsO₄·2H₂O)), as well as some interaction between the phases. New insight into the mechanisms of removal and the materials chemistry will be discussed along with the aging effects on the materials and on the compositional ratio of As(III) and As(V) ions in the floc.

9:20am AS+SS-TuM5 Evolution of Metal-Core Oxide-Shell Iron Nanoparticles as a Function of Time in an Aqueous Environment, D.R. Baer, Pacific Northwest National Lab; P.G. Tratnyek, Oregon Health and Sciences Univ.; J.E. Amonette, C.M. Wang, M.H. Engelhard, Pacific Northwest National Lab; Y. Qiang, University of Idaho; J.T. Nurmi, V. Sarathy, Oregon Health and Sciences Univ.; J. Antony, University of Idaho

The high reactivity of metallic iron nanoparticles with contaminants such as chlorinated hydrocarbons, the possibility of solution based delivery to contamination zones and evidence of an ability of the nanostructure to alter reaction pathways have stimulated considerable research into the potential use of iron metal nanoparticles for environmental remediation. As part of our study of the chemical properties of nanoparticles, we are examining how metal-core oxide-shell iron nanoparticles evolve with time in aqueous environments. X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and x-ray diffraction (XRD) are used to examine the particles at different times after exposure to water solutions with and without carbon tetrachloride. The influence of formation, processing and analysis conditions on the nature of the core/shell structure has been examined in some detail. The room temperature oxidation of these nanoparticles shows the formation of voids and in some circumstances hollow oxide nanoparticles. Other measurements show that an electron beam damages the oxide shell allowing oxidation to occur in the normal environment of a TEM. Aspects of particle reactivity have been examined by batch reactivity, electrochemical and electron paramagnetic resonance measurements. Studies measuring the reductive dechlorination of carbon tetrachloride (CT) have shown that nanoparticle properties (as well as solution chemistry and other experimental conditions) affect the distribution of products formed. Of particular interest are factors that favor degradation of CT by product formation pathways that do not produce chloroform (CF), which is a persistent and toxic byproduct.

9:40am AS+SS-TuM6 Effects of Dopant Concentration and Microstructures on Ionic Conductivity in Samaria Doped Ceria Thin Films, Z.Q. Yu, Nanjing Normal University; C.M. Wang, M.H. Engelhard, D.E. McCready, V. Shutthanandan, R. Shao, PNNL; P. Nachimuthu, UNLV; O. Marina, I. Lyubinskyy, L.V. Saraf, S. Thevuthasan, PNNL

Recently, samaria doped ceria (SDC) have received much attention in the literature due to its high ionic conductivity and high oxygen ion transport, and they are considered to be the most promising solid electrolytes for the intermediate temperature solid oxide fuel cells (SOFCs). Although SDC materials show promising results, there are controversies regarding the dopant concentration that provide higher values for ionic conductivity. The discrepancies in ionic conductivity are mostly due to different sample preparation methods and the crystalline quality associated with these methods. In addition, high quality single crystal ceria thin film work with dopants is limited in the literature. In this study, we have investigated the ionic conductivity as a function of samarium dopant concentration in high quality samaria doped ceria films that were grown on sapphire (0001) substrates using oxygen plasma assisted molecular beam epitaxy (OPA-MBE). The structural properties of these films were characterized using in situ reflection high energy electron diffraction (RHEED) and exitu glancing angle x-ray diffraction. Thickness along with the compositional analysis was carried out using Rutherford backscattering spectrometry and x-ray photoelectron spectroscopy depth profiling. Microstructures in the films and at the interfaces were investigated by high resolution transmission electron microscopy (TEM) and TEM micrographs show sharp interfaces without grains and film/substrate epitaxial relationship as CeO@sub 2@ (111)// alpha-Al@sub 2@O@sub 3@ (0001) and CeO@sub 2@ [110]// alpha-Al@sub 2@O@sub 3@ [-2110]. Total conductivity measurements clearly show that the conductivity in these films is significantly higher than that in the polycrystalline material with the maximum values for the samarium concentration of 11 cation %. We will discuss these results along with the effects associated with grain boundaries in conductivity in these films.

10:40am AS+SS-TuM9 Getting Atomic-Scale Information from Complex Surfaces using Synchrotron Radiation, D.P. Woodruff, University of Warwick, UK **INVITED**

"Chemical shifts" in core-level photoelectron binding energies are an important feature of conventional laboratory-based x-ray photoelectron spectroscopy (XPS) and indeed are why the technique was originally referred to as ESCA - electron spectroscopy for chemical analysis. For surface studies, however, this ability to exploit XPS chemical shifts is greatly enhanced through the use of modern synchrotron radiation facilities to

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achieve enhanced spectral resolution and surface specificity. There are now many examples of how such core level shifts alone can distinguish and give insight into the nature of adsorbed and coadsorbed species on surfaces. In addition, however, these chemically-shifted photoemission peaks can be used to provide quantitative chemical-state-specific local structural information by using them to monitor photoelectron diffraction and absorption in x-ray standing waves. For both methods the high spectral brightness, tunability, and ability to provide light in the vacuum ultra-violet and soft x-ray ranges are essential features provided only by synchrotron radiation. These capabilities will be illustrated by a small number of case studies of adsorption and coadsorption systems where the ability to distinguish atoms of the same element in different chemical or structural local environments proved essential to understanding the systems.

11:40am AS+SS-TuM12 X-ray Spectrometry with the NIST Transition Edge Sensor Microcalorimeter, *T. Jach, N.W.M. Ritchie, J. Ullom*, National Institute of Standards and Technology

We report on the use of the NIST Transition Edge Sensor Microcalorimeter to obtain high-resolution x-ray spectra over extended energy ranges for materials analysis. The microcalorimeter is a detector with dimensions of 400 μm x 400 μm oper deposited by individual photons by means of a resistive sensor ated at a temperature of 70 mK. It detects the energy operating at its superconducting-normal transition. The resolution of the detector is determined by the energy range for which it is designed. Our current detector has demonstrated a resolution of 4.4 eV over an energy range of 7 keV. The spectra were obtained from samples excited by the high-energy electron beam in an electron microprobe. We have performed quantitative analyses on two NIST reference glasses in which we are able to characterize the concentrations of multiple elements to an accuracy of less than 2%. The resolution of the lines in their spectra was such that we are able to identify the transitions in a series and their satellites. In transitions where the initial state is the valence band, our energy resolution is starting to allow identification of features in the density of states. We foresee detectors which will permit the chemical identification of species in x-ray fluorescence similar to what is now done with ESCA, but without the need for ultra high vacuum.

12:00pm AS+SS-TuM13 Dynamical XPS Measurements, *A. Dana, S. Suzer*, Bilkent University, Turkey

Photoelectron spectra of a clean silicon sample and another one containing 10 nm oxide layer are recorded while the sample rod is subjected to 10.0 V square pulses with varying frequencies in the range of 0.001 to 1000 Hz to probe the dynamical response of the samples. For the clean silicon sample the Si2p(Si0) peak is twinned and appears at correspondingly -10.0 eV and +10.0 eV binding energy positions (20.0 eV difference) at all frequencies measured. However, although the Si2p (Si4+) of the oxide is also twinned, the measured difference between the peaks is smaller than 20.0 eV and exhibits a strong frequency dependence due to charging of the oxide layer. The frequency dependence of the oxide layer can be experimentally simulated by the clean silicon tied through an external RC circuit. The frequency dependent shifts of the peaks, their broadening, and other related experimental parameters can be reproduced by modeling the various currents involved as a voltage controlled current source to yield a powerful extension of XPS for dynamical measurements of charging/discharging processes of surface structures. As a simple application of the technique we will show that the two O1s components, which can be assigned to SiOx and TiOy domains in a composite film, exhibit different dynamical behavior. Other applications fro probing dielectric properties of various surface structures will be presented and discussed.

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Applied Surface Science

Room 2005 - Session AS-WeM

Molecular Ion Sources and Characterization of Biomaterials

Moderator: J. Shallenberger, Evans Analytical Group

8:00am AS-WeM1 Recent Advancements in Polymeric Depth Profiling with an SF₅⁺ Cluster Primary Ion Source, C.M. Mahoney, National Institute of Standards and Technology INVITED

The utility of cluster Secondary Ion Mass Spectrometry (SIMS) for depth profiling applications in polymeric materials has been repeatedly demonstrated in the past decade, where it has been used to obtain molecular and fragment information as a function of depth in several polymer systems. In addition to homopolymers, polymeric blends, multilayers and copolymer systems have been successfully characterized as a function of depth. Finally, the capability to monitor the in-depth distribution of small molecules embedded in organic and polymeric matrices has been realized. This talk will describe the ongoing research efforts at NIST to further develop cluster SIMS as a tool for polymer surface and in-depth characterization. Results indicate that SF₅⁺ is a promising tool for polymer depth profiling, and with the right set of conditions, including temperature, sample rotation and selection of analysis source, one can obtain optimal results. Mahoney, C.M.; Roberson, S.V.; Gillen, G. *Anal. Chem.* 2004, 76, 3199-3207. Mahoney, C.M.; Yu, J.X.; Gardella, J.A. *Jr. Anal. Chem.* 2005, 77 (11), 3570-3578. Wagner, M.S. *Surf. Interface Anal.* 2005, 37(1), 42-70. Wagner, M.S. *Anal. Chem.* 2005, 77(3), 911-922. Chen, J.; Winograd, N. *Anal. Chem.* 2005, 77(11), 3651-3659.

8:40am AS-WeM3 TOF-SIMS Analysis of C60 Sputtered Organic Thin Films, S.R. Bryan, J. Moulder, G.L. Fisher, Physical Electronics; N. Sanada, ULVAC-PHI

Sputtering of organic materials using a C60 ion beam has been demonstrated to produce significantly less accumulated damage compared to sputtering with atomic ion beams. This has opened up the possibility of sputtering organic materials while maintaining the organic structural integrity at the bottom of the crater. We have studied C60 sputtering for several years using XPS. This has led to a better understanding of the optimum sputting conditions. In this presentation we will present new data on TOF-SIMS analysis of C60 sputtered organic films. By combining the quantification and atomic bonding information from XPS with the longer range structural information from TOF-SIMS, a better understanding of the C60 sputtering process will emerge.

9:00am AS-WeM4 XPS and QCM Studies of PMMA and Teflon AF1600 Films Bombarded by 1-20 keV C₆₀⁺ Ions, I.L. Bolotin, S.H. Tetzler, L. Hanley, University of Illinois at Chicago

C₆₀⁺ ions are widely used as projectiles in secondary ion mass spectrometry of polymeric materials. Evidence exists that the mechanism of sputtering by C₆₀⁺ ions allows their use for damage-free depth profiling. Surface analysis studies are presented to probe absolute sputtering yields and surface modification of two polymer films by C₆₀⁺ ions. Polymethylmethacrylate (PMMA) and Teflon AF1600 spin-casting films studied during different bombardment doses of C₆₀⁺ ions with energies of 1-20 keV by quartz-crystal microbalance (QCM) and X-ray photoelectron spectroscopy (XPS). Measurements for the total sputter yield of films are acquired using a QCM. Mass-lost rate data show that each 20 keV C₆₀⁺ cluster leads to emission ~10⁶ amu of polymer, indicating that the non-overlapping crater regime exists for doses of 10 keV. Chemical modification is also probed by XPS of the target surface before and after ion bombardment. Both polymers display little to no damage to their film structure at ion fluences below ~10¹³ ion/cm². Changes in C 1s XPS spectra during higher fluence bombardment can be explained predominantly by differential charging effects. However, ion fluences >10¹⁵ ion/cm² modify the film composition to a carbon-rich material with various degradation products.

9:40am AS-WeM6 Applications of a Bismuth-Cluster Ion Gun in Organic and Inorganic Surface Analysis, F. Kollmer, R. Moellers, T. Grehl, D. Rading, E. Niehuis, ION-TOF GmbH, Germany

In recent years primary ion clusters are increasingly applied for the analysis of organic surfaces by TOF-SIMS. Since they increase the secondary ion

formation efficiency by orders of magnitude cluster sources are replacing the mono-atomic primary ion sources more and more. As primary ion species a large variety of different clusters as Au_n⁺, Bi_n⁺, C_n⁺, C₆₀⁺, SF₅⁺, ... are applied. Possible drawbacks of cluster sources are the applicable cluster currents (measurement time) and the achievable performance with respect to lateral resolution and mass resolution. Recent advances in molecular surface analysis were made by the application of cluster liquid metal ion sources (LMIG) operated with Au or Bi. These sources combine the fundamental benefits of cluster ion bombardment with a high brightness source capable to achieve a high performance with respect to lateral resolution and mass resolution. In particular the Bi source shows interesting aspects as a large variety of emitted singly and doubly charged ions, high cluster currents, and the ability to operate at very low emission currents. At low emission currents the energy spread of the emitted species is reduced which improves the achievable lateral resolution. In this contribution we address fundamental capabilities of the Bi cluster source as the composition of the emitted primary ion beam, the energy spread of the ions, the stability of the source and the influence of the emission current on these. We applied Bi cluster ions to organic surfaces for micro area analysis and imaging with high lateral resolution. We also found new interesting applications of Bi clusters for inorganic surface analysis and dual-beam depth-profiling.

10:40am AS-WeM9 Utilization of Polymers in Ocular Science Applications, R.M. Braun, Bausch & Lomb INVITED

The healthcare industry, as a whole, has seen the rapid incorporation of polymeric materials into a variety of devices in recent years. This progression along the development trail has led to a multitude of life-changing products that range from convenience items like liquid bandages to prostheses that repair damaged joints and teeth. Moreover, we can not forget the life-saving products like stents and heart valves, nor the pharmaceutical products that rely on polymers to regulate dosing within a given application. Clearly, the use of polymers within biomaterial applications has become widespread and will likely continue to expand as time progresses. Although advancements in the ocular sciences industry are not often highlighted in the same light as those noted above, contributions toward improving patient health and the quality of life through materials development are abundant. These facts have recently come to light with the aging population associated with the baby-boomer generation. The products and applications within this industry include contact lenses and associated comfort solutions, replacement lenses for cataract issues and pharmaceutical products that treat back of the eye diseases that can lead to blindness. While these industry sectors are too large to discuss completely, this talk will highlight a few biomaterial related systems associated with the human eye and touch on some of the challenges associated with surface analytical measurements.

11:20am AS-WeM11 Multi-Technique Characterization of a Drug Delivery System to Obtain 3-D Chemical Information, A.M. Belu, Medtronic, Inc.; C.M. Mahoney, National Institute of Standards and Technology; K. Wormuth, SurModics, Inc.

Medical devices are increasingly being designed to incorporate drug delivery. For example, drugs are currently incorporated into catheters to reduce microbial infection, placed on stents to prevent restenosis of the artery, and incorporated into pacing lead tips to prevent inflammation of heart tissue. As more drug delivery systems are being created, it is important to characterize their properties, and relate the properties to how the system will function in the human body. This study focuses on the characterization of a rapamycin/PLGA delivery system on a stent. The goal is to understand the lateral and depth distribution of the drug in the polymer film. The information can then be used to predict the release profile of the drug in vivo. Several different formulations of rapamycin/PLGA were studied (5, 25, 50% drug, and 25% with a capcoat). The surface composition of the films were characterized and quantified by ESCA and TOF-SIMS. Information on drug concentration from the surface towards the bulk of the film was determined by depth profiling by SIMS with a cluster ion source. To determine the distribution of drug/polymer species in the bulk of the film in the x-, y-, and z-direction, confocal Raman was used. In the films with high concentration of drug, individual clusters of drug on the order of a few microns were resolved. The data from the multiple methods of characterization will be compiled to allow a fuller understanding of the delivery systems. The strengths and weaknesses of each of the characterization techniques will be compared.

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11:40am **AS-WeM12 Combining Fluidics, Surface Chemistries and Direct Mass Spectrometric Detection to Address Protein Analyte Quantitation from Complex Samples for the Purpose of Diagnostic Assays**, *L.O. Lomas, E. Fung, E. Boschetti*, CIPHERGEN

The development of analyte assays for the purpose of diagnostic tests is driven by multiple factors, including sample availability, required throughput and quantitative reproducibility. Although antibody-based assays have dominated in the detection of peptide/protein analytes and serve well in terms of throughput and quantitative reproducibility, mass spectrometry is becoming more main-stream due to the added information provided in terms of precise analyte conformation by mass and/or secondary structure fragmentation. Laser Desorption/ionization mass spectrometry (MS) is particularly well suited for both peptide and protein characterization, however, absolute quantitation has been elusive due to complexities associated with integrating sample processing and final analyte detection. To resolve these issues, we have integrated unique solid-phase extractions chemistries directly on MS probes that allow us to quantitatively extract the protein analytes of interest from a complex sample in a defined and controlled process. The resulting analyte arrays minimize the sample requirements and allow for high-throughput processing using standard sample fluidic systems. To exemplify this process, we describe the development of a seven protein-marker panel that may aid in the stratification of women with a pelvic mass. The specific MS-based analyte array assays permit the discrimination of post-translationally modified forms of the markers and by using reference standards, we are able to achieve absolute quantitation with high reproducibility (CV<10%). The integrated assay platform includes an automated liquid handler, analyte-specific arrays, and a MS reader. Measurements of the seven markers provide a measure of the risk that a pelvic mass is malignant. Women at low risk for ovarian cancer can be further evaluated by their general gynecologist, while women at high risk for ovarian cancer should be evaluated by a specialist gynecologic oncologist.

12:00pm **AS-WeM13 The Surface Characterisation of Arrayed Biomaterial Systems**, *A.J. Urquhart*, University of Nottingham, UK; *D.G. Anderson*, Massachusetts Institute of Technology; *M.R. Alexander*, University of Nottingham, UK; *R. Langer*, Massachusetts Institute of Technology; *M.C. Davies*, University of Nottingham, UK

In recent years the increase in interest in combinatorial materials science, via high throughput synthetic techniques, has attracted considerable interest mainly in the facilitation of rapid discovery and the optimisation of functional polymeric biomaterials. Critical to the selection of a biomaterial to a specific clinical application is the relationship between polymer interfacial chemistry and biological response. However, there has been to date few reports addressing the challenge of studying the interfacial chemistry of high throughput arrays with high spatial resolution. Here we report, for the first time, on the surface characterisation of a novel polymer array, comprising of 572 polymer species (each polymer spot being approximately 300 μm in diameter) and fabricated by the Anderson et al. method, using X-ray photoelectron spectroscopy (XPS), time of flight secondary ion mass spectrometry (ToF-SIMS), water contact angle (WCA) and atomic force microscopy (AFM). In order to maximise the information obtained from the large data sets principal component analysis was applied to observe trends between polymer composition and stem cell adhesion/proliferation on the arrays. D. G. Anderson, S. Levenberg and R. Langer, *Nature Biotechnology*, 2004, 22, 863.

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Room 2005 - Session AS+BI-WeA

Imaging and Characterization of Biological Materials

Moderator: L.J. Gamble, University of Washington

2:00pm **AS+BI-WeA1 Imaging Biomolecules at Surfaces, R.M.A. Heeren, E.R. Amstalden, A.F.M. Altelaar, M. Froesch, L.A McDonnell**, FOM-Institute for Atomic and Molecular Physics, The Netherlands

INVITED

Mass spectrometry is one of the technologies that enable the investigation of the spatial organization of biomolecules at complex surfaces. The potential of imaging MS as a biomedical imaging technique is evident. Direct biomarker visualization on tissue is only one of a few key applications. Imaging mass spectrometry is currently undergoing rapid developments in areas spanning the entire technology chain required to generate a mass resolved chemical image. New detection technology and novel imaging approaches improve speed, sensitivity and spatial resolution of imaging MS. In this contribution we will discuss several technological and methodological aspects of imaging mass spectrometry using a set of selected applications in biomedical imaging. Various approaches exist that use different incarnations of imaging mass spectrometry ranging from protein profiling to high resolution imaging using MALDI and SIMS. In our studies, a novel stigmatic or microscope mode imaging MS strategy is employed that allows for the rapid generation of high resolution, large field-of-view mass resolved images of cells and tissue. This mass microscope is combined with tissue digestion strategies that aid in the identification of larger proteins found in tissue section. One of these strategies involves the so-called molecular scanner, a technique where proteins are electro-blotted from the tissue through a membrane containing immobilized proteolytic enzymes. While the proteins pass through the membrane they are digested into smaller proteolytic peptides that are subsequently captured on a PVDF membrane. This technology enhances the detection sensitivity as multiple peptides are generated from a single protein molecule. The advantages of this high resolution imaging approach, using the molecular scanner will be demonstrated on cervical tissue sections obtained in the framework of a biomarker discovery study for cervical cancer.

2:40pm **AS+BI-WeA3 Acquisition of Chemical Information from Cell Samples Using TOF-SIMS Imaging, D. Breitenstein**, TASCION GmbH, Germany; **C. Rommel, J. Wegener**, University of Münster, Germany; **R. Moellers, E. Niehuis**, IONTOF GmbH, Germany; **B. Hagenhoff**, TASCION GmbH, Germany

Our ongoing studies focus on the mass spectrometric imaging for cells, an emerging area in TOF-SIMS research. In a joint research effort we want to elucidate the transport mechanism for drugs through the blood-liquor barrier. Being a vacuum technique TOF-SIMS faces some challenges for the analysis of epithelial cells. A standard approach to maintain the cellular integrity of cells during the experiments is freeze fracturing or cryomicrotomy. However, these techniques increase the experimental effort significantly. As we were not interested in the lateral distribution of elemental species like Na or K but small and middle sized molecules we concentrated on different fixation techniques instead. Mainly, paraformaldehyd and glutardialdehyd were used. In order to visualize the three-dimensional molecular structure of the cells C@sub 60@ sputtering was combined with imaging using Bi@sub 3@ primary ions. In order to compare the results with a standard analytical technique in biochemistry, additionally cells were treated with fluorescent dyes. The intact fluorophores could be detected successfully in the TOF-SIMS images. The obtained mass resolved images for the fluorescent dyes were compared successfully with the widely accepted technique of confocal laser scanning microscopy (CLSM), proving the validity of the chosen mass spectrometric approach. This work was supported by the German Federal Ministry for Education and Research (Grand: 0312002B).

3:00pm **AS+BI-WeA4 Complementary Application of SIMS and CARS for Biochemical Imaging of Cells and Tissues, D.W. Moon**, Korea Research Institute of Standards and Science, Korea; **T.G. Lee, E.S. Lee, J.Y. Lee**, Korea Research Institute of Standards and Science; **J.W. Shim**, AmorePacifc Corporation; **J.W. Kim, K.W. Kim**, Seoul National University, Korea

There have been significant progresses in analysis of biomolecules on surfaces using surface analysis tools such as XPS, SIMS, SPR, and FT-IR. Major demands of biosurface analysis come from DNA chips, protein chips, and surface modification for tissue engineering. However, cell physiologists and medical and pharmaceutical scientists prefer in-vitro analyses of biomolecules in live single cells and tissues in spite of technical difficulties

to biochemical assays. In this presentation, we report our recent studies on 2D or 3D label-free biochemical imaging of various cells and tissues such as liver, skin, retina, and hair based on complementary use of coherent anti-Stokes Raman scattering (CARS) and SIMS. TOF-SIMS measurements are based on cluster ion bombardment such as Au₃, Bi₃, and C₆₀ and CARS measurements are optimized for the C-H vibration of biomolecules in live cells and tissues. CARS showed clear C-H chemical bond specific images with 300 nm spatial resolution and 1 μm depth resolution down to 100 μm depth, revealing detailed tissue structures in the sub-cellular level without any damage problems. SIMS showed much more surface sensitive and specific biomolecular mass images with some depth profiling capabilities. The present status and the future prospect of complementary use of CARS and SIMS with sensitivity and selectivity improvement based on a broad band spectrum and cluster bombardment, respectively will be discussed for practical applications in disease diagnostics and cell and tissue based drug screening.

3:20pm **AS+BI-WeA5 Desorption Electrospray Ionization: Fundamentals and Applications in Surface Analysis and Biological Imaging, R.G. Cooks, Z. Takats, J.M. Wiseman, D. Ifa, N. Talaty, A. Jackson, A. Venter**, Purdue University

INVITED

This talk concerns ambient ionization using desorption electrospray ionization (DESI) and the related methods. These procedures allow direct analysis of biological samples, including proteins and lipids, on surfaces or in tissue without sample preparation. Biological fluids can also be examined directly, or by adsorption on a matrix like paper. DESI is suitable for characterization of both large and small molecules and it combines features of electrospray ionization (ESI) with those of the family of desorption ionization (DI) methods. It allows organic molecules present on surfaces to be analyzed by mass spectrometry without requiring that the sample be introduced into the vacuum system of the mass spectrometer. DESI has high sensitivity, is virtually instantaneous in response time, and there is little or no sample preparation. The sample is sprayed with charged microdroplets of water or a simple organic solvent. The sample remains fully accessible to observation as well as additional physical and chemical processing during the analysis. Applications to metabolomics, to high throughput analysis of pharmaceutical preparations, to drugs and drug metabolites in blood, serum and other biological fluids, are described. Tissue imaging is demonstrated with lipids being used as biomarkers to search for disease and in-vivo sampling of living tissue surfaces is described. Laser doppler anemometry is used to characterize the DESI mechanism. It is shown that at least two major processes are involved. One involves transfer of molecules from the surface to the droplet projectiles, the other involves proton or other charge transfer from the slow-moving projectile to the sample molecule. Variations on the DESI method in which reactive compounds are included in the spray solvent allow recognition of specific functional groups.

4:00pm **AS+BI-WeA7 Characterization of Bacterial Spores using Nano-Secondary Ion Mass Spectrometry (NanoSIMS), S. Ghosal, S.J. Fallon**, Lawrence Livermore National Laboratory; **T. Leighton, K. Wheeler**, Children's Hospital Oakland Research Institute; **I.D. Hutcheon, P.K. Weber**, Lawrence Livermore National Laboratory

Bacterial spores are elementally zoned at the nanometer scale. This zonation may be controlled by spore physiology, physical factors, and elemental diffusion. Here we present a recently developed nanometer-scale secondary ion mass spectrometry (NanoSIMS) technique that allows the direct visualization and quantification of elemental concentration gradients within spores. By using NanoSIMS depth profile analysis together with sample preparation techniques such as focused ion beam (FIB) sectioning, we are able to probe the three dimensional elemental distribution within individual *Bacillus thuringiensis israelensis* (Bti) spores with nanometer scale resolution (~10 nm depth and 50 nm lateral). Our results show the expected distributions for physiologically controlled elements (Ca, P) and provide baseline data other elements (e.g., Li, F, Cl, S). We also demonstrate cation and anion mobility in spores under hydrous conditions. Our results suggest a permeation mechanism by which elements diffuse into and out of the spore along hydration pathways on rather short time scales. Additional studies are in progress to define the rates and mechanisms controlling ion mobility in spores. @FootnoteText@ @footnote@This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-4.

Wednesday Afternoon, November 15, 2006

4:20pm **AS+BI-WeA8 Vacuum Ultraviolet Postionization for Mass Spectrometry of Small Molecule Analytes in Bacterial Biofilms**, *L. Hanley, P.D. Edirisinghe, M. Zhou*, University of Illinois at Chicago; *K.A. Skinner-Nemec, C.S. Giometti*, Argonne National Laboratory; *J.F. Moore*, MassThink; *J.E. Hunt, W.F. Calaway, M.J. Pellin*, Argonne National Laboratory

Mass spectrometric analysis and imaging of intact microbial biofilms are difficult with established methods. A new experimental strategy is discussed for analyzing small molecule analytes within intact biofilms: laser desorption followed by postionization with 7.87 eV radiation of molecular analytes whose ionization potentials have been lowered by chemical derivatization with an aromatic tag. Postionization mass spectrometry with derivatization is developed on small peptides with aromatic or native tags such as a tryptophan residue. The new method is then applied to the detection of a quorum sensing peptide in a *Bacillus subtilis* bacterial biofilm. Finally, detection of an antibiotic is demonstrated by direct 7.87 eV postionization, without derivatization. These mass spectrometric methods show promise for the study of antibiotic resistance in microbial biofilms as well as other studies of small molecule analytes within complex biological matrices. P.D. Edirisinghe et al., *Anal. Chem.* 76 (2004) 4267. L. Hanley et al., *Appl. Surf. Sci.* (2006), in press.

4:40pm **AS+BI-WeA9 Chemical and Biological Differentiation of Human Breast Cancer Cell Types Using Time-of-Flight Secondary Ion Mass Spectrometry**, *K. Kulp, E. Berman, M. Knize, J. Felton, E. Nelson, J. Montgomery*, Lawrence Livermore National Laboratory; *L. Wu, D. Shattuck*, University of California, Davis; *K. Wu*, Lawrence Livermore National Laboratory

We use time-of-flight secondary ion mass spectrometry (TOF-SIMS) to image and classify individual cells on the basis of their characteristic mass spectra. Using statistical data reduction on the large data sets generated during TOF-SIMS analysis, similar biological materials can be differentiated on the basis of a combination of small changes in protein expression, metabolic activity and cell structure. We apply this technique to image and differentiate three carcinoma-derived human breast cancer cell lines (MCF-7, T47D, and MDA-MB-231). In homogenized cells, we show the ability to differentiate the cell types as well as cellular compartments (cytosol, nuclear, and membrane). These studies illustrate the capacity of TOF-SIMS to characterize individual cells by chemical composition, which could ultimately be applied to detect and identify single aberrant cells within a normal cell population. Ultimately, we anticipate characterizing rare chemical changes that may provide clues to single cell progression within carcinogenic and metastatic pathways.

Thursday Morning, November 16, 2006

Applied Surface Science

Room 2005 - Session AS-ThM

Ultra Thin Films and Buried Interfaces

Moderator: F.A. Stevie, North Carolina State University

8:00am **AS-ThM1 Deep Core X-ray Photoelectron and Auger Spectra: A Comparison of Different Methods for Interpretation**, *L. Kövér*, Institute of Nuclear Research of the Hungarian Academy of Sciences, Hungary; *M. Novák*, Institute of Nuclear Research of the Hungarian Academy of Sciences; *S. Egri*, University of Debrecen, Hungary; *I. Cserny*, *Z. Berényi*, *J. Tóth*, Institute of Nuclear Research of the Hungarian Academy of Sciences; *W. Drube*, Synchrotron DESY, Germany; *F. Yubero*, CSIC-U, Spain; *S. Tougaard*, University of Southern Denmark; *W.S.M. Werner*, Vienna University of Technology, Austria

The accuracy of quantitative chemical analysis of surface/interface layers is significantly influenced by the spectral contribution from electrons suffered energy losses within the solid. There is little information on the effects of such loss processes for higher energy electrons, promising for analysis of buried interfaces. Deep core (1s, 2s) photoelectron and KLL Auger spectra (resonant and non-resonant) excited by hard X-rays from homogeneous semiconductors Si, Ge and 3d transition metals (Cu, Ni, Fe) were measured with high energy resolution. The measured spectra were analyzed applying different approaches: i) the spectra were fitted by components reflecting surface, bulk and intrinsic (hole induced) excitations, using the "modified Hüfner model", ii) by the help of the Partial Intensity Analysis method contributions from bulk and surface excitations were successively removed from the spectra, iii) the spectra were simulated using the dielectric response theory. For surface excitations, both former models yield only small contributions to the spectra, while using the dielectric response theory surface and bulk excitations are not separated. Strong deviations occur, however, regarding the contribution from intrinsic excitations estimated by using different models, especially between the dielectric response theory and the other two models. Possible reasons of these deviations are discussed. This work was supported by the European Community - Research Infrastructure Action under the FP6 'Structuring the European Research Area' Programme (through the Integrated Infrastructure Initiative) Integrating Activity on Synchrotron and Free Electron Laser Science. @FootnoteText@ @footnote 1@L. Kövér, M. Novák, S. Egri, I.Cserny, Z. Berényi, J. Tóth, D. Varga, W. Drube, F. Yubero, S. Tougaard, W. S. M. Werner, Surf. Interface Anal. 38(2006)569. @footnote 2@W. S. M. Werner, Surf. Interface Anal. 31(2001)141. @footnote 3@F. Yubero, S. Tougaard, Phys. Rev. B71(2005)045414.

8:20am **AS-ThM2 Film Thickness Determination of Ultra Thin HfO₂ Dielectrics with Angle Resolved XPS**, *W.S.M. Werner*, *W. Smekal*, Vienna University of Technology, Austria; *D.W. Moon*, Korean Research Institute for Standards and Science, Korea; *K.J. Kim*, Korean Research Institute for Standards and Science, Republic of Korea; *C.J. Powell*, National Institute of Standards and Technology

Reflection electron energy loss spectra (REELS) have been measured for medium energy (300-3400 eV) electrons reflected from solid Si, SiO₂ and HfO₂-surfaces. The normalized differential probability for surface and volume excitations was extracted from these data. Furthermore, the total inelastic mean free path (IMFP) for volume scattering as well as the total surface excitation probability (SEP) for a single surface crossing were determined. Measured angle-resolved XPS spectra of thin HfO₂ films on amorphous Si were analyzed using the experimental electron scattering data. The experimental spectra were compared with model calculations using the SESSA software providing a verification of the commonly employed models for overlayer thickness determination with XPS. Guidelines are given for the optimum experimental conditions and parameters to use in the analysis of angle resolved XPS measurements of ultrathin dielectric films. @FootnoteText@ W. Smekal, W. S. M. Werner and C. J. Powell, Surf. Interface Anal. 37(2005)1059 @footnote 2@ <http://www.nist.gov/srd/nist100.htm>

8:40am **AS-ThM3 Structure and Properties of Ultra-Thin SiO₂ Plasma Polymer Films at Polymer/Metal Interfaces**, *T. Titz*, *K. Wapner*, *G. Grundmeier*, Max-Planck-Institut fuer Eisenforschung, Germany

This film surface engineering is one of the key interests of the flat metal producing industry to fabricate ultra-thin functional films in a continuous process. The requirements range from corrosion protection of the surface to a specific control of the physical, optical and electronic properties of the

surface. Grundmeier et al. studied in detail the nucleation and growth, wettability and barrier properties of protective plasma polymers on metals. @footnote 1-3@ In the presented work, ultra-thin silica like films have been deposited on zinc and zinc alloy model substrates by plasma polymerization in a microwave plasma reactor. The chemical composition of the films was measured by means of Fourier transform infrared reflection-absorption spectroscopy (FT-IRRAS) as well as X-ray Photoelectron Spectroscopy (XPS). The topography of the plasma polymer films was mapped by atomic force microscopy (AFM). Current density-potential curves for the measurement of the kinetics of the oxygen reduction and electrochemical cyclic voltammetry for the analysis of the redox properties of the plasma modified passive film were performed. Scanning Kelvin Probe studies reveal the electronic properties of the buried interface between the plasma polymer and the metal oxide interface. A clear inhibition of the ion and the electron transfer reactions at the buried interface was found even at very low film thickness. @FootnoteText@ @footnote 1@ G. Grundmeier, P. Thiemann, J. Carpentier, N. Shirtcliffe, M. Stratmann, Thin Solid Films, 446 (2004) 61. @footnote 2@ V. Barranco, J. Carpentier, G. Grundmeier, Electrochim. Acta, 49 (2004) 1999. @footnote 3@ G. Grundmeier, P. Thiemann, J. Carpentier, V. Barranco Surf. Coat. Tech., 174 (2003) 996.

9:00am **AS-ThM4 Interfacial Interactions of PEKK Polymer Coatings onto Oxide-free Phosphate Films on an Aluminum Surface**, *A.L. Asunskis*, *P.M.A. Sherwood*, Oklahoma State University

In a series of papers we have shown how thin (10nm or less) oxide free phosphate films can be formed on a number of metals. The films formed have potential as corrosion resistant films. We have also shown that it is possible to extend the range of the surface coatings that can be formed by placing a thin polymer layer over the phosphate layer. In this paper we show how the water insoluble polymer poly(ether ketone ketone), PEKK can be placed over a thin oxide free phosphate film on aluminum metal. The surface and the interfaces involved were studied by valence band and core-level X-ray photoelectron spectroscopy (XPS). Difference spectra in the valence band region were used to show that there is a chemical interaction between the PEKK and phosphate thin films on the aluminum metal. Three different phosphate film compositions were studied using different phosphorous containing acids, H₃PO₄, H₃PO₃, and H₃PO₂. This type of interaction illustrates the potential of phosphates to act as adhesion promoters. The valence band spectra are interpreted by calculations.

9:20am **AS-ThM5 DualBeam and Electron Microscopy Characterization of Buried Interfaces**, *L.A. Giannuzzi*, FEI Company **INVITED**

A DualBeam instrument is a focused ion beam (FIB) column and a scanning electron microscope (SEM) on the same platform. The synergistic combination of FIB and SEM enables both 2D and 3D characterization of buried interfaces where site specific precision and throughput may be critical. Interphase interfaces as well as internal interfaces (i.e., grain boundaries) often govern material behavior and properties. Direct DualBeam characterization as well as DualBeam specimen preparation for subsequent transmission electron microscopy (TEM) or scanning TEM (STEM) is often the only way to characterize, monitor, or study the failure analysis mechanisms of buried interfaces, especially where nanometer scale devices or material multi-layers exist. Examples of techniques, methods, and applications of DualBeam characterization and specimen preparation of buried interphase interfaces and grain boundaries will be presented.

10:00am **AS-ThM7 Applications of ToF-SIMS Depth Profiling to Problems Involving Buried Interfaces and Particulate**, *K.G. Lloyd*, The DuPont Experimental Station

Buried irregular interfaces and particulate present special challenges in terms of chemical analysis and identification, and yet are critically important to diagnose in the manufacture of electronic materials and devices. Cross-sectioning at the right location is often difficult, and, while dual-beam SEM/FIB instruments can often provide excellent visualization of buried defects, matching chemical analysis may be absent or problematic. ToF-SIMS depth profiling, with its ability to acquire spatially-resolved depth profiles while collecting an entire mass spectrum at every "voxel", offers a way to re-visit the problem of buried defects. Unlike traditional dynamic SIMS applications, the emphasis will be on the qualitative, not the quantitative. Multivariate analysis of the overwhelming amount of data can reduce the output from essentially a depth profile at every mass to a small set of chemically-meaningful factors. Examples of

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ToF-SIMS depth profiles of relatively homogeneous layers, severely inhomogeneous layers, and buried particulate will be discussed.

10:20am **AS-ThM8 Vacuum Splitting at Buried Electronic Interfaces: A Technique Enabling Nanoscale Chemical and Physical Analysis**, *W.F. Stickle*, Hewlett-Packard Company; *D. Ohlberg, J.J. Blackstock, C.L. Donley, D.R. Stewart*, Hewlett Packard Labs

In modern solid-state electronic devices, the critical layers and interfaces are now reaching scales of only a few nanometers thick. These layers are generally buried underneath thick and complex materials stacks, the fabrication of which frequently alters the chemical and physical properties of the critical interfaces. Nonetheless, correlating the chemical and physical structure of these nanoscale layers and interfaces is essential for optimizing reliable device performance. The conventional approaches for analysing deeply buried layers employ ion-milling to depth-profile the materials stack down to the critical film or interface. However, such depth-profiling processes often induce chemical and physical changes several nanometers below the exposed surface. This modification of the device stack can reduce the utility of such investigations -- particularly when the critical interfaces are of chemical compositions or physical structures that are easily altered by atom bombardment. We present a novel method for investigating the undamaged physical and chemical properties of buried critical layers and interfaces. This technique is based on engineering a weakened interface adjacent to the layer(s) of interest in the device stack, followed by physical cleaving at this interface in a UHV environment. We present UHV XPS and STM data from a series of experimental nanoelectronic device stacks investigated with this new method, and compare the data against those acquired using conventional depth-profiling. Direct comparison illustrates the utility of this new method for acquiring accurate information on the physical and chemical structure of buried nanoscale layers and interfaces.

10:40am **AS-ThM9 SIMS Measurements of C contamination in SOI**, *M.H. Yang, L. Wang, L. Li*, Evans Analytical Group

SIMS have been shown as a powerful technique to distinguish SOI metal contamination and dopant distributions on surface, in the upper Si layer, in the BOX and at the BOX/Si substrate interface with excellent detection limits. C measurements in SiO₂ has been a challenge for SIMS because in situ carbon absorption in the oxide during SIMS measurements. With improved charge neutralization and special treatment of SOI sample surface including advanced polishing, we are able to achieve C detection in SiO₂ at ~1E+17 atoms/cm³ for samples with SOI thickness greater than 10 microns. We are also able to reduce the surface C tailing effect by an order of magnitude, and achieve better detection of C in the SiO₂ BOX and their interfaces for samples with thickness less than 100nm. Partial support by Texas Advanced Technology Program of THECB #003656-0029-2003.

Electronic Materials and Processing

Room 2003 - Session EM+AS-ThM

High-k Dielectric Characterization

Moderator: A. Rockett, University of Illinois, Urbana-Champaign

8:00am **EM+AS-ThM1 A Study of High Dielectric Constant Magnesium Oxide Film Interfaces with Si**, *L. Yan, R.P. Shrestha, E.A. Irene*, University of North Carolina-Chapel Hill; *L. Zhong, I. Kim, O. Auciello*, Argonne National Lab

In a recent report we have identified MgO as a potential high dielectric constant (ϵ) gate dielectric because of its chemical inertness enabling sharp interfaces and wide band-gap (7.3 eV) for large band offsets with silicon (Si) to minimize leakage. Our prior investigation of reactively sputtered MgO on Si revealed impressive interfacial electronic properties as compared with the conventional SiO₂/Si, in particular comparable interface trap densities (D_{it}). The present study is aimed at a closer exploration of MgO thin films, prepared using two different oxidizing agents: molecular and atomic oxygen on reactively

sputtered Mg. In situ XPS, Mass Spectrometry of Recoiled Ions (MSRI) and spectroscopic ellipsometry (SE) were used to monitor the evolution of the interfaces with MgO. This, coupled with post-deposition, ex situ cross-sectional TEM, provided an accurate materials description of the MgO/Si interface. Electronic measurements, including capacitance versus voltage (C-V), conductance ($G(\omega)$) versus gate voltage ($G(\omega)-V$), and current flux versus electric field (J-E), were conducted on capacitor structures to determine ϵ , D_{it} , and leakage current, respectively. Our results show that thin MgO films can provide a superior ϵ dielectric for many electronic applications. This work is supported by the National Science Foundation (NSF) Materials Research Division.

8:20am **EM+AS-ThM2 Channel Drift Mobility in High-k Transistors from Galvanomagnetic Measurements**, *R.T. Bate, W.P. Kirk, R. Agrawal*, University of Texas at Arlington; *R.M. Wallace, B.E. Gnade, G. Pant*, University of Texas at Dallas

Effective mobility μ_{eff} in high-k transistors can be degraded by enhanced scattering of carriers and by trapping. The drain current is proportional to the product of the channel carrier density n and the drift mobility μ , and the capacitance measurement used to determine channel carrier density cannot distinguish between free and trapped charge. The result is that trapping can cause μ_{eff} to underestimate μ . We combine Hall effect and magnetoresistance (MR) measurements to determine μ of carriers in the channel. Then effective mobility reductions due to increased scattering can be separated from loss of carriers due to trapping. In the past, Hall effect measurements have been used to measure Hall mobility in MOSFET and MISFET channels, and μ has been estimated by making assumptions about the magnitude of the Hall factor r_H which is the dimensionless ratio of the Hall mobility to the drift mobility, (i.e. $r_H = \mu_H/\mu$). r_H is usually assumed to be close to unity. Theory indicates that r_H is strongly dependent on the type of carrier scattering in the channel, which is usually not known a priori. This uncertainty is currently the main drawback of the Hall effect as a means of determining channel drift mobility. We propose to use the MR to estimate r_H . Analysis based on the silicon 100 inversion layer shows that the MR is strongly correlated with r_H , regardless of the scattering mechanism. This is being experimentally verified on MOSFET structures where r_H and μ can be independently determined, and the results are being carried over to high-k MISFETs. Knowing r_H permits μ to be estimated, not only from Hall measurements, but also, for routine diagnosis, from MR measurements on conventional transistors (not Hall devices), even in the presence of significant trapping. Partial support by Texas Advanced Technology Program of THECB #003656-0029-2003.

8:40am **EM+AS-ThM3 Interface Composition and Band Alignment in Nano-electronics**, *S. Rangan, E. Bersch, R.A. Bartynski, L.V. Goncharova, T. Gustafsson, E. Garfunkel*, Rutgers University

INVITED

We outline some key issues relevant to characterization of interfaces in next-generation highly-scaled CMOS devices. Selected experimental results as well as conceptual approaches to addressing the structure, bonding and band alignment problems will be discussed. The semiconductor/high-K and high-K/metal interfaces will be the primary focus of the discussion. Ion scattering, photoemission, inverse photoemission, electron microscopy, and other methods have been used to examine (i) amorphous high-K gate dielectrics and their interfaces on Si, Ge and GaAs, (ii) epitaxial oxides on Si, and (iii) metal-dielectric interfaces for gate metallization. From a comparison of experimental and theoretical results we are able to develop a better understanding of the electronic properties of the different structures. We find that the band gap, barrier height and dielectric response of this class of materials are very phase-dependent. An understanding and control of band alignment for charge injection and carrier confinement must be realized if novel materials are to be incorporated in future nano-electronic devices.

9:20am **EM+AS-ThM5 Band Offsets Measurements of Metal/High-k/Semiconductor Structures**, *S. Rangan, E. Bersch, R.A. Bartynski, E. Garfunkel*, Rutgers University

The study of high-k dielectrics and metal gate electrodes has been ongoing in order to thoroughly understand the properties of these materials and to contribute to their implementation in Metal/Oxide/Semiconductor Field Effect Transistors. The band offsets are an important property of Metal/Oxide/Semiconductor (MOS) stacks in that the leakage current depends directly on them. An understanding of the band offsets, particularly the role played by the interface dipole, may enable the

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development of tunable band offsets at the interfaces. We have used in situ photoemission and inverse photoemission as well as synchrotron photoemission to measure the band offsets between the layers of MOS stacks. UV, X-ray, and inverse photoemissions give us a direct measurement of the bandgap of the dielectric and offsets between dielectric and semiconductor bands. With sequential metallization (Al, Ru, Ti) shifts of the band edges are measured as a function of metal coverage. The band offsets we measure for the metal/oxide and oxide/semiconductor interfaces are, to first order, in good agreement with the modified Schottky Mott model which treats the interface with bare bulk (metal, oxide or semiconductor) properties. But as expected, photoemission reveals much more complicated interfaces, and in particular strong effects on the chemistry of the entire stacks upon metal deposition. We report here the energy gap and band offsets of several Hf_xSi_{1-x}O₂ oxides on a Si substrate, as well as the effect of Ru (high work function metal) and Al (low workfunction metal) deposition on these dielectrics. Both Ru and Al induce an energy shift of the core levels (Hf4f, Si2p), the valence and conduction bands – the shift depends both on the oxide and on the metal choice. Ru stays metallic upon deposition on the oxide, whereas Al is shown to be oxidized even at room temperature. We will show that the source of oxygen can be the dielectric or the interface layer between the substrate and the oxide.

9:40am **EM+AS-ThM6 A Soft-X-Ray Photoelectron Spectroscopy Study of D-State Contributions to Valence Band States in Nanocrystalline HfO₂, TiO₂, and Hf_{1-x}Ti_xO₂ Alloys**, *L.B. Fleming, M.D. Ulrich*, NC State University; *J. Rowe*, University of North Carolina at Chapel Hill; *C.C. Fulton, G. Lucovsky*, NC State University

This paper compares d-state contributions to valence band, and valence band edge defect states determined from i) synchrotron soft x-ray photoelectron spectroscopy (SXPS) at photon energies between 40 and 80 eV, with d-state contributions determined from ii) ultra-violet photoemission spectroscopy (UPS) at 21.2 eV. Measurements have been performed on thin films of HfO₂, TiO₂ and Hf_{1-x}Ti_xO₂ alloys prepared by reactive evaporation, and subjected to post deposition annealing at 700°C. The atomic Hf, Ti and O contributions to the valence band states in the SXPS and UPS spectra are at approximately the same energies with respect to the Fermi level, but have different spectral weighting. The only significant differences in the USP and SXPS spectra are defect state features at, and above the valence band edge. The UPS spectra, limited by the incident photon energy, yield a single feature with a spectral peak ~1 eV above the valence edge, whereas SXPS spectra, performed with higher incident photon energies can defect electronic states deeper into the forbidden band gap. The SXPS spectra confirm the band edge features, as well as identifying a second defect states at higher energy, ~3 eV above the valence band edge. The defect states in TiO₂, and the alloys are interpreted in as O-atom vacancy states in which the formal valence of Ti is 3+ rather than 4+. This assignment is based on comparisons between SXPS spectra, and epsilon₂ spectra obtained from analysis of reflection spectra of TiO₂ over a spectra range from 0.01 eV to 10 eV. Defect states in HfO₂ are similar, and assigned to d-states of Hf³⁺ at O-atom vacancies.

10:00am **EM+AS-ThM7 Line-Width and Symmetry Changes in Jahn Teller Term-Split Sc 3d-States in LaScO₃ as a Function of Deposition and Annealing Temperatures**, *H. Seo*, NC State University; *L.F. Edge, D.G. Schlom*, Penn State University; *N.A. Stoute, G. Lucovsky*, NC State University
LaScO₃ conduction band states are derived in part from Jahn-Teller-split Sc 3d-states in distorted octahedral arrangements of O-neighbors. Conventional XRD for films deposited at ~300°C, and annealed to 700°C display no evidence for crystallinity, while films annealed to >800°C display strong crystalline features. New studies of conduction band states by i) vacuum ultra-violet spectroscopic ellipsometry (VUV SE), and ii) x-ray absorption spectra (XAS) for transitions from (a) spin-orbit split Sc 2p core states (Sc L_{2,3}) and (b) the O 1s core state (O K₁), are compared, providing insights into scales of order. XRD results are indicative of grain sizes >5 nm for >800°C anneals, but do not distinguish between i) amorphous films, and ii) nanocrystalline films with grain sizes

10:20am **EM+AS-ThM8 Trends in Core Level Binding Energies of Mixed Oxide Candidates for High-κ Dielectrics**, *A. Mathew*, University of Delaware; *L. Bao*, Dupont Inc.; *K. Demirkan*, University of Delaware; *C.-G. Wang, G.D. Wilk*, ASM America Inc.; *R.L. Opila*, University of Delaware
Hafnium silicates and lanthanum aluminates are among the many proposed candidate materials for replacing the SiO₂ gate dielectric

in transistors for low standby power applications. Photoelectron spectroscopy with its sensitivity to local chemical bonding is an invaluable tool for investigating these interfaces. Hafnium silicates were deposited using Atomic Layer Chemical Vapor Deposition (ALCVD@super TM@), and the lanthanum aluminates were sputter deposited. Systematic trends in core level binding energies are observed for the unannealed mixed oxide systems as a function of composition. The degree to which such shifts occur is seen to be a function of both the amount of charge transfer between the component cations as well as the local lattice potential, both initial state effects. The O 1s photoemission peak and the N 1s peak (in the case of nitrified films) reflects the local bonding environment in the film, and its variations with different concentrations of a number of cations are studied as well. The O 1s and N 1s peaks can be deconvoluted into components arising from its bonding with a higher or lower electronegativity cation, and their relative intensities vary with composition. These insights into the local bonding structure are important for improving our capability to engineer the ideal semiconductor / high-κ interface for optimal device performance.

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Applied Surface Science

Room 2005 - Session AS-ThA

Combined Methods or Multiple Methods

Moderator: I.S. Gilmore, National Physical Laboratory

2:00pm **AS-ThA1 A Fundamental Investigation of Erucamide Migration in Polyolefin Matrices**, *J. Chen, B. Walther, J. Li, T. Hu*, The Dow Chemical Company

Erucamide is the most widely used slip agent in plastic manufacturing processes. It is well known that erucamide migrates toward the surface leading to a reduction in the coefficient of friction (COF), but not much has been published on the details of the surface migration. Our study has shown that the surface layer of erucamide is a function of many factors including the matrix material and thickness, temperature shelf time and other factors. X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF SIMS), atomic force microscopy (AFM) and other technologies were applied to develop fundamental understanding of the erucamide migration mechanism and the correlation with COF. This paper will discuss our fundamental investigations of surface migration of erucamide through polyolefin resins.

2:20pm **AS-ThA2 Phenomenological Relationships Between Chemistry and Mechanical Properties Derived from ToF-SIMS and Nanoindentation Observations**, *G.L. Fisher*, Physical Electronics; *C. Szakal, N. Winograd*, The Pennsylvania State University; *J.G. Swadener*, Los Alamos National Laboratory

Remarkable correlations between the chemistry and the mechanical properties of polytetrafluoroethylene (PTFE) have been revealed as a function of ionizing radiation fluence. Specifically, changes in the hardness are explained in terms of the macromolecular evolution during α particle (5.5 MeV $^{4}\text{He}^{2+}$) irradiation. Chemical changes in the surface region of the polymer, i.e. macromolecular evolution, were evaluated using a ToF-SIMS instrument that was equipped with a 20 keV C^{60+} ion probe. The mechanical properties of hardness and elastic modulus were monitored in the near-surface ($\sim 2.5 \mu\text{m}$) region of the polymer by nanoindentation. Nanoindentation shows that scissioning of the linear polymer chains by α particles is offset by crosslinking at moderate doses and leads to a peak in the elastic modulus at $\sim 10^8$ Rad. The elastic modulus falls off with continued irradiation due to an increase in molecular mobility that arises by a reduction in the average molecular weight of the matrix molecules (i.e. fragmentation). The magnitude of the hardness indicates that crosslinking continues to a dose of $\sim 5 \times 10^9$ Rad and thereafter declines with continued irradiation due to fragmentation. The ToF-SIMS data also reveal a peak in the level of crosslinking at $\sim 5 \times 10^9$ Rad that is followed by extensive fragmentation of the matrix molecules. In contrast to nanoindentation, the method by which ToF-SIMS data is used to evaluate the relative degree of crosslinking in a polymer matrix is immature. Therefore, the molecular fragments that were evaluated, the mechanism(s) by which they arise in the mass spectrum, and the treatment of the data will be discussed. These developments represent a significant step forward in the application of ToF-SIMS to address the properties of soft materials.

2:40pm **AS-ThA3 Multi-technique, Multivariate Analysis Methods for Enhanced Sample Characterization**, *J.E. Fulghum, K. Artyushkova, S. Pylypenko, J.L. Fenton, K.M. Archuleta*, University of New Mexico; *L. Williams*, University of New Mexico

INVITED

Characterization of heterogeneous samples frequently requires multi-technique correlations. The ability to acquire images from the same area on samples using multiple techniques provides opportunities for enhanced sample characterization, including using data from one technique to facilitate or confirm interpretation of data from a second technique. A variety of techniques, including AFM, FTIR, XPS and confocal microscopy (CM) have comparable fields-of-view, although spatial resolution and information content differ dramatically. This talk will incorporate a variety of examples of multi-technique correlations including visualization of 3-D polymer chemistry through correlation of XPS, CM and AFM data; fusion of high spatial resolution AFM images with high energy resolution XPS images for enhanced spatial distribution information; quantification of CM image data sets through fusion with XPS quantitative images, and correlation of AFM images with contact angle data. Correlating the data from multiple techniques, as in the examples listed above, requires matching and marking of the sample analysis areas, image registration, multivariate image analysis, image quantification and image fusion. We are currently

developing a Matlab-based Graphical User Interface (GUI), that includes all of these steps. The goals of the GUI include managing images from multiple modalities, performing multiple imaging processing steps such as classification and PCA, segmentation, image registration, image fusion, volume reconstruction; providing tools that support flexibility by incorporating new and existing image analysis routines; and providing a simple, yet powerful user interface. The current status and availability of the GUI will be described.

3:20pm **AS-ThA5 Multi-Technique Characterization of Niobium Surfaces for Superconducting Radio Frequency (SRF) Accelerators**, *H. Tian*, College of William & Mary; *C.E. Reece*, Thomas Jefferson National Accelerator Facility; *M.J. Kelley*, College of William & Mary, US; *S. Wang, L. Plucinski, K.E. Smith*, Boston University; *M.M. Nowell*, Edax Tsl

The accelerator structure for the proposed International Linear Collider (ILC) comprises more than 20,000 Nb cavities operating at 2 K, and having a total internal surface area in excess of 16,000 m². Upgrade of Jefferson Lab's CEBAF accelerator from 6 GeV to 12 GeV is about to begin. It will require 80 new cavities and will be preceded by refurbishment of about 40 of the original 338. Other applications of RF superconductivity to particle accelerators are being actively explored. The shallow microwave penetration (with local electric fields exceeding 55 MV/m) causes superconducting RF accelerator performance to be strongly influenced by the chemistry, topography and structure of the top several nanometers of the internal surface. These are substantially determined by post-fabrication etching and conditioning. We examined single and polycrystal Nb material, etched by chemical polishing and electropolishing and post-treated by extended low-temperature baking at ultra high vacuum condition which are commonly used for cavity production. The combined use of XPS, synchrotron-based (variable photon energy) photoemission, atomic force microscopy (AFM), stylus profilometry and electron backscatter diffraction (EBSD) provides key insights into the effect of post-fabrication treatments on the Nb surface. The improved knowledge of materials aspects of RF superconductivity provides a stronger foundation for future major accelerator projects. H. Tian, J. Padamsee, J. Knobloch, T. Hays; RF Superconductivity for Accelerators, Wiley, New York, (1998).

3:40pm **AS-ThA6 Ion Sputtering and the Static Limit for Nanoparticles**, *D.J. Gaspar, Z. Zhu, A.S. Lea, D.R. Baer, M.H. Engelhard*, PNNL

The behavior of nanomaterials varies in many cases from that observed for bulk materials. During the course of studies on several types of particles and nanostructured materials, we have observed evidence that the extent of damage and material removal rates due to ion sputtering may be significantly different than for continuous films or bulk forms of similar materials. This presentation will review our efforts to quantify the sputter and damage rates for some particle and nanomaterial systems, including salt particles, iron oxide, titania and ceria nanoparticles and nanoporous silica films. Additionally, we have attempted to correlate measurement of SIMS damage cross-sections in measurements of titania nanoparticles with other measurements of particle structure and chemistry, including Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and X-ray Photoelectron Spectroscopy (XPS). For the data presented here, material removal rates are monitored directly by profilometry, and indirectly by TOF-SIMS, XPS and Auger Electron Spectroscopy (AES). For large aggregates of nanoparticles, TOF-SIMS spectra appear the same as bulk materials. We have extended these measurements to TiO_2 nanoparticles dispersed by chemical attachment to self-assembled monolayers. We suggest the contributions of geometric factors and energy transfer modified by nanoscale features contribute to observed variations in sputter rates. We examine the relationship of our observations to theoretical efforts including the theory of Bradley and Harper and Monte Carlo simulations of nanoscale effects on sputtering. D.J. Gaspar, et al., Surf. Interface Anal., 37 (2005) 417-423. D.R. Baer, et al., J. Surf. Anal., 12 (2005) In press. R.M. Bradley, R.M. and J.E. Harper, J. Vac. Sci. Technol. A 6 (1988) 2390. Jurac, S., et al., Astrophys. J., 503 (1998) 247-252.

4:00pm **AS-ThA7 Optimised XPS Depth Profiling of Aluminium Surfaces**, *C. Blomfield, A.J. Roberts*, Kratos Analytical Ltd, UK; *J.C. Walmsley*, Sintef, Trondheim Norway

Characterization is a key activity within aluminum surface science technology. Corrosion and protection mechanism studies are one of a number of areas of study that also include coatings, joining processes,

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chemical processing, lubrication, rolling and extrusion. The behavior of trace and impurity elements in aluminum alloys is of interest and it is essential to have effective surface characterization tools to study these. Surface and near-surface segregation studies of model aluminum alloys will be used to illustrate the complementary information that can be obtained from different techniques and how this can be related to the properties of the surface. A combination of low-energy ion gun technology, small area analysis, sample rotation and increased instrumental sensitivity have come together to make XPS particularly suited to analysis of the role of trace elements in surface segregation.

4:20pm AS-ThA8 Characterization and Metrology Challenges in SiON Gate Thin Films for ULSI Technology, G. Conti, C. Lazik, Y. Uritsky, T.C. Chua, C. Czarnik, Applied Materials; S.R. Bryan, Physical Electronics; T. Gustafsson, E. Garfunkel, Rutgers University

Silicon oxynitrides (SiON) films are presently used as a replacement of SiO₂ gate dielectric film in oxide semiconductor field effect transistor MOSFET. SiON films can be grown by a variety of processes such as: thermal oxynitridation, low energy ion implantation, chemical vapor deposition, and atomic layer deposition. Depending on the growth process and the process parameters, nitrogen can pile up at or near the Si/SiO₂ interface, be uniformly distributed throughout the film, or be enriched at the interface of the poly-Si gate electrode. The N distribution significantly affects the electrical properties of the gate dielectric layer; therefore, during process development the physical properties of the SiON film (thickness, composition, and atomic depth distributions) must be determined. Whereas most of the analytical techniques become less effective as film thickness drops towards the 10Å range, angle resolved x-ray photoelectron spectroscopy (AR-XPS) becomes a very effective technique in this range. AR-XPS is capable of providing precise thickness and detailed information on elemental and chemical composition. However, extracting a depth distribution from the data requires calculating the angular response for trial models and comparing to the data. Since a fit is not a guarantee of trustworthy, AR-XPS depth profiles results were compared to other surface techniques. We characterized "golden standard" samples for N dose and N profile by TOF-SIMS, and by MEIS, and compared the results to AR-XPS. TOF-SIMS instead predicted a broad and flat profile even for box-like profiles created by CVD and it does not capture any distinct SiO₂ layer beneath the SiN layer. MEIS agrees with AR-XPS fit confirming our ability to measure depth-profile non destructively. In addition, preliminary results from TEM/EELS analysis agree with AR-XPS and MEIS results.

4:40pm AS-ThA9 Ultimate Nanoprobing in UHV: Four independent Scanning Tunneling Microscopes Navigated by High Resolution UHV SEM, M. Maier, J. Westermann, T. Berghaus, Omicron NanoTechnology GmbH, Germany

A major challenge in Nanotechnology is the incorporation of single nano-devices into larger integrated circuits. Traditional instrumentation suffers from one fundamental issue: How to cover the dimensional range of a fully integrated circuit down to the nanometer range (or even atomic scale) of single devices and have an adequate integrated navigation system. To meet these requirements, we have established and being advancing a new approach to integrating state-of-the-art SPM technology via high resolution electron microscopy and spectroscopy: (1) Bridging dimensions and rapid navigation; (2) Combining different surface analysis methods at the very same sample area to gain complementary information; (3) Integrated position-readout of sample and probe positioning; (4) Pushing each single technology to its inherent limits. The system facilitates four independent Scanning Tunneling Microscopes and the UHV version of the Zeiss Gemini SEM column with ultimate resolution below 4nm for probe navigation and rapid localisation of sample features or devices. STM imaging is used to pro-actively position and contact the probe(s) on nano-devices. Using STM probe approach technology, a controlled electrical contact is ensured to finally perform a four-point measurement on the nano-scale. Beyond navigation, SEM enables different electron spectroscopy methods to gain magnetic or chemical information on the sample area. Using SEMPA (SEM with polarization analysis) magnetic domain imaging with a resolution in the 10nm range is achieved to allow for correlation of transport properties and domain distribution. Using SAM (Scanning Auger Microscopy) chemical mapping can be achieved with 10nm resolution to correlate transport properties and material composition. Various application examples will be shown to illustrate the system capabilities.

Biomaterial Interfaces

Room 2014 - Session BI+AS-ThA

Biomolecule-Surface Characterization I

Moderator: J.S. Shumaker-Parry, University of Utah

2:00pm BI+AS-ThA1 Nanostructured Titanium Surfaces for Bone Biotemplating Applications, K.C. Papat, T. Desai, University of California, San Francisco

A major goal in orthopaedic biomaterials research is to design implant surfaces which will enhance osseointegration in vivo. Several micro as well as nanoscale architectures have been shown to significantly affect the functionality of bone cell i.e. osteoblasts. In this work nanotubular titania surfaces fabricated by a simple anodization process were used as templates for culturing osteoblasts. The size of nanotubes can be controlled by varying the voltage and the time of anodization. Marrow stromal cells were isolated from rat and were seeded on nanotubular titania surfaces along with control surfaces. Cell adhesion, proliferation and viability were investigated for up to 7 days of initial culture. The cells were then provided with differentiation media to induce matrix production. The alkaline phosphatase activity and matrix production were quantified using a colorimetric assay and X-ray photoelectron spectroscopy (XPS) for up to 4 weeks of culture (3 weeks after providing differentiation media). Further, scanning electron microscopy (SEM) was used to investigate osteoblast morphology on these nanotubular surfaces.

2:20pm BI+AS-ThA2 Nonlinear Optical Studies of Transmembrane Polypeptide Incorporation into Supported Bilayer Membranes, D. Levy, K.A. Briggman, National Institute of Standards and Technology

The structure and organization of proteins in biological membranes play critical roles in cellular functions related to recognition and signal transduction. Supported bilayer membranes (SBMs) have been developed as model membrane systems for the characterization of biomolecular interactions at cell surfaces. In the present study, the nonlinear interface-specific technique of vibrational sum-frequency spectroscopy (VSFS) is used to characterize the thermal phase transition for both single and binary component lipid layers in SBMs. The incorporation of alpha-helical transmembrane polypeptides into SBMs has also been characterized by VSFS and infrared spectroscopy to determine the insertion kinetics, structure and orientation of the polypeptides into the various SBMs.

2:40pm BI+AS-ThA3 Analysis of In-Vitro Biomineralization Processes Quantitatively by Quartz Crystal Microbalance (QCM)- and Transmission Electron Microscopic (TEM)- Explorations, U. Plate, Ch. Mentrup, H.J. Hoehling, Universitaet Muenster, Germany

The primary crystallites of different developing hard tissues describe an apatitic structure with crystal lattice fluctuations representing an intermediate state between amorphous and fully crystalline. Some non-collagenous proteins (NCPs) bound immobilized at the surface of collagen type I are implicated in the initiation and regulation of crystal formation and growth. In the investigations we have induced synthetic biomineralization processes. Collagenous matrices were reconstituted in-vitro and Phosvitin, a Phosphoprotein from an eggshell, were used (concentration 6 mg/ml in 0,3M Na₂CO₃). Phosvitin was cross-linked to collagen type I fibrils (concentration 0,25 mg/ml in 0,05M HAc) with Divinylsulfon (DVS). Dynamic in-vitro biomineralization processes at this matrices, pure collagen and Collagen-DVS-Phosvitin, were induced by contacting their surfaces with defined inorganic Ca- and PO₄-solutions. Qualitative and quantitative measurements were achieved in an in-vitro model for Quartz Crystal Microbalance (QCM)- and Transmission Electron Microscopic (TEM)- explorations. To locate the organic matrix for QCM- and TEM- measurements statistically, the Au-surfaces on the quartz- and TEM-grids were functionalised with thiols containing chain-length carboxylic-acid groups, in the experiences 10 µM carboxylic-acid thiols with a mercaptopropyl group. This carboxylic-acid groups form self assembling monolayers (SAMs) and are utilized for the modification of an Au-surface to introduce carboxylic groups on it. Then the carboxylic groups are converted to amines of biomaterials. To induce biomineralisation processes 2,2 mM CaCl₂- and 1,3 mM K₂HPO₄-solutions were pumped along the matrices in defined time intervals with a peristaltic pump. The experiments were carried out in a chamber under native conditions (T = 37°C, pump velocity of the Ca-phosphate solutions of 1,62 ml/min, comparable to the fluid flux of blood in capillaries.).

Thursday Afternoon, November 16, 2006

3:00pm **BI+AS-ThA4 Study of the Interfacial Water Structure on Sulfobetaine-Terminated Thiolate Self-Assembled Monolayers**, *M.J. Stein, B.D. Ratner*, University of Washington

The foreign body response to prosthetic devices limits the extended use of virtually all medical implants and biosensors. Non-specific protein adsorption is believed to be a key determinant of this response. To circumvent or control these reactions, our initial study utilized a zwitterionic sulfobetaine thiol, structurally similar to taurine (HS(CH₂)₂)₁₁N(CH₂)₃)₂CH₂SO₃⁻), and diluted it with hydrophobic and hydrophilic thiols to determine whether the nonfouling ability of the sulfobetaine self-assembled monolayers (SAMs) could be enhanced by either an improved packing of its bulky headgroup or through an increase in the internal hydrophilicity of the thiol monolayer. In our current study, we hypothesized that the diluted groups that were previously shown to be the most nonfouling would exhibit more structured water (~3200 cm³/m³) versus free water (~3400 cm³/m³). For this study, attenuated total reflectance (ATR) was utilized to characterize changes in the water peak signal intensity through a full time-series of dilutions at multiple temperatures. Initial results have shown that a trend is present that mirrors the earlier protein adsorption results and that this trend follows a time-dependant pattern.

3:20pm **BI+AS-ThA5 Multi-Technique Characterization of Lipid/PEG Interactions and Oligonucleotide Microarrays**, *H.J. Griesser*, University of South Australia, Australia; *K. Vasilev, B. Thierry, K. Bremmell, S. Griesser, P.-C. Nguyen*, University of South Australia; *P. Hale, P. Pigram*, LaTrobe University, Australia

INVITED
This contribution will discuss two recent studies utilizing multi-technique characterization of surfaces by both vacuum spectroscopic methods and in contact with aqueous solutions. The first study aimed to investigate why PEG graft surfaces have produced excellent protein resistance in vitro but disappointing outcomes in vivo. Our hypothesis was that a possible reason involves attractive interfacial interactions with lipids that then provide a platform for subsequent protein adsorption. Using three different proin-resistant PEG coatings it was indeed found that two of them gave measurable lipid adsorption. Using lipid molecules that were neutral, positively charged, or negatively charged, and aqueous media of various ionic strengths, we explored the possible role of electrostatic interactions. Interaction force measurements using the AFM colloid probe method showed purely repulsive steric forces on approach, but on retraction adhesive forces were observed in some cases. A key issue is to differentiate between interfacial forces that emanate from the substrate and 'shine through' the PEG graft layers, and forces associated with the PEG layer itself. The second study involves the fabrication of micro-patterned surfaces and their use for oligonucleotide and protein microarrays. Using a mask with circular holes we plasma polymerize arrays of dots consisting of thin layers of plasma polymers that carry reactive groups (aldehyde, amine, or epoxy) suitable for covalent immobilization of end-functionalized oligonucleotides or proteins. XPS imaging using a Kratos Ultra unit with a DLD clearly showed the arrays of dots on perfluoropolymer substrate and the immobilization of biomolecules. An IonTOF ToF-SIMS unit with a Bi³⁺ beam was used to analyze immobilized oligonucleotides. Clearly identifiable peaks were observed with masses up to 2,500 Da and higher, from fragments as large as containing five nucleotides. Different oligonucleotides could be distinguished by the distinct fragmentation patterns.

4:00pm **BI+AS-ThA7 Effects of Annealing and Sample Processing Methods on Surface Molecular Orientation of Ultra-high Molecular Weight Polyethylene**, *S. Sambasivan, D.A. Fischer, M.C. Shen, J.A. Tesk, S.M. Hsu*, National Institute of Standards and Technology

Ultra-high molecular weight polyethylene (UHMWPE) has remained the dominant polymer in artificial joints due to its outstanding wear resistance properties. It has been demonstrated in the past that the molding and annealing the ultra-high molecular weight polyethylene (UHMWPE) at a safe elevated temperature resulted in increased mechanical strength. Also, cross-linking of UHMWPE has been shown to reduce wear significantly. This novel study utilizes resonant absorption of linearly polarized soft x-rays at a synchrotron beamline to characterize the molecular orientation of the UHMWPE surface layer (top 10 nm) which is understood to be a precursor to wear. Carbon-K-edge x-ray absorption measurements were done on the UHMWPE samples, which were annealed in nitrogen atmosphere. Effects of annealing and cross-linking on the wear characteristics were also examined. It was found that the degree of orientation after annealing the sample at 130°C in nitrogen, the average molecular orientation in

UHMWPE decreased significantly (about 80% reduction) compared to the un-annealed UHMWPE. These studies show a promising new insight into how UHMWPE wears and will aid in the development of new materials for artificial joints. In addition to the annealing and cross-linking studies, it was observed that routine surface preparation methods such as molding, polishing and microtoming also induced surface molecular orientation to various degrees.

4:20pm **BI+AS-ThA8 NanoTribological Studies on the Mechanisms of O-Linked Glycosylated Proteins in the Boundary-Lubrication of Articular Cartilage**, *S. Zauscher, N.I. Abu-Lail, D. Chang, F. Guilak*, Duke University; *G. Jay*, Brown University

The diarthroidal (synovial) joints of the body enable locomotion and activity while withstanding millions of loading cycles, which may be several times body weight. Recent macroscopic tribological experiments and biochemical analyses suggest that heavily glycosylated proteoglycans, encoded by gene proteoglycan 4 (PRG4) and expressed by synoviocytes in synovial fluid as lubricin and by chondrocytes on the superficial zone of articular cartilage as surface zone protein (SZP), provide boundary lubrication in cartilage in the absence of interstitial fluid pressurization. We will present results from nanotribo-mechanical measurements on model surfaces and cartilage, combined with other surface specific physicochemical measurements that shed new light on the mechanisms by which lubricin/SZP provides lubrication and wear protection in diarthroidal joints. Our results suggest that the role of effective boundary lubricants in mediating friction in articular joints is largely one of wear protection of surface asperities, maintaining the surfaces in a nonadhesive mode, and causing shear dissipation in the biopolymeric boundary lubricant layer, even at the cost of attaining "high" coefficients of friction (COF ~ 0.15). Lubricin's ability to form intermolecular disulfide bonds appears to be critical for its ability to develop large steric repulsion forces. Our results contribute significantly to the understanding of the conformation and physico-chemical function of mucinous glycoproteins on biological interfaces.

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Applied Surface Science

Room 3rd Floor Lobby - Session AS-ThP

Aspects of Applied Surface Science Poster Session

AS-ThP1 TOF-SIMS Analysis of pH Dependent Structure of Protein-A Immobilized on ITO Coated Substrate, N. Kato, M. Higuchi, Seikei University, Japan; S. Aoyagi, Shimane University, Japan; M. Kudo, Seikei University, Japan

It is known that the environmental conditions, such as pH and temperature, control the reactivity of the protein immobilized on the biosensor surface. For example, at pH < 3.0, protein-A which is used as antigen for immunosensor can not bind to immunoglobulin-G (IgG). In contrast, for pH = 7.0, protein-A can bind to IgG. To explain this difference on reactivity, it is important to examine the structural change of protein-A caused by varying pH condition. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is one of the most useful techniques for the investigation of biomaterial surfaces because of its ability to provide detailed molecular information on material surfaces. However the TOF-SIMS spectra of protein samples are very complex with multiple fragments resulting from each of the 20 amino acids. It was shown that information theory can select the appropriate peaks of secondary ions characterizing samples out of numerous candidate peaks in the TOF-SIMS spectra with the calculation of mutual information.¹ In this study, the structural change of protein-A caused by varying pH condition was analyzed by TOF-SIMS with the information theory and principal component analysis (PCA). PCA of the TOF-SIMS spectra from protein-A immobilized on ITO coated glass showed explicit distinction between the chemical structures at pH=7.4 and pH=3.0. The calculation of mutual information for TOF-SIMS spectral data at the two pH conditions provided specific peaks related to protein-A at each pH condition. From comparison between the variation of the specific peaks at each pH condition and the amino acid sequences of Protein-A, the structural change of protein-A caused by varying the pH condition will be discussed. ¹S. Aoyagi, M. Hayama, U. Hasegawa, K. Sakai, M. Tozu, T. Hoshi, M. Kudo, *J. Surf. Sci. Nanotech.* 1, 67 (2003).

AS-ThP2 ToF-SIMS as a Reliable Tool for Cyanobacterial Toxic Molecules Research, C. Bittencourt, H. Sarmento, J.-P. Descy, J.-J. Pireaux, L. Houssiau, University of Namur, Belgium

In a previous work¹ we have demonstrated that ToF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry) is a reliable tool to probe bixin, a natural carotenoid used as food colorant, present in bixa orellana seeds. In this work, we have applied the technique to the analysis of cyanobacterial toxic molecules. Toxin production by cyanobacteria is a prominent research topic due to the increasing occurrence of these organisms following eutrophication and global warming as well as due to its association with human diseases such as amyotrophic lateral sclerosis/Parkinsonism dementia complex (ALS/PDC). Among several toxins that threaten the current life microcystins and β -N-methylamino-L-alanine (BMAA) come into view as important cases of studies due to their proximity to human life. To assess the specific hazards of cyanobacterial toxic molecules it is necessary to understand their chemical and physical properties. We show that ToF-SIMS can be used as an important complementary tool in the characterization of cyanobacterial toxic molecules. Standards were studied in order to obtain reference spectra. We found that the parent molecules are readily detected by means of (M) and (M+1) molecular ions. The spectra recorded on the BMAA exhibit high intensity peak m/z 118, which can be related to the parent molecule along with mass ions fragments which can be understood from the molecular structure. Similar results were found for Microcystin-LR; the parent molecule at m/z 995.56 and its related fragments. The sensibility of the ToF-SIMS to analyze cyanotoxins shows that this technique is a potential tool for its analysis. ¹L. Houssiau, M. Fellicissimo, C. Bittencourt and J.J. Pireaux, *Appl. Surf. Sci.* 231-232 (2004) 416.

AS-ThP3 High Resolution Mass Spectrometric Analysis of Non-Dehydrated Biological Samples, H.F. Arlinghaus, J. M@um o@ller, C. Kriegeskotte, D. Lipinsky, Universit@um a@t M@um u@nster, Germany

ToF-SIMS and laser-SNMS are increasingly important tools for analyzing the elemental and molecular distribution in biological samples. However, in-vivo analyses of tissues or cell cultures are impossible because the sample must accommodate the vacuum conditions of the instrument. Thus, fixing the sample in its vital state, such as freezing, is essential. Sample preparation by cryofractioning or cryosectioning techniques followed by

freeze-drying has been successfully used. However, these techniques exhibit several limitations. In order to overcome these limitations, a combination of a ToF-SIMS/laser-SNMS instrument and an in-vacuum cryosectioning instrument was developed for directly preparing and analyzing frozen non-dehydrated samples. In our presentation, we will discuss various sample preparation techniques for analyzing cell cultures and tissue samples and the possibility of obtaining 3D molecular images of frozen biological samples. Particularly, we will show that the analysis of frozen non-dehydrated samples with an in-vacuum preparation technique for exposing the interesting layers of the sample and creating pristine surfaces offers several advantages in comparison to techniques using freeze-dried samples. However, the analysis of cold samples may lead to problems with especially H@sub 2@O adsorption onto the cold surfaces. This is avoided by using a special temperature treatment. Our analysis showed that increasing the temperature to around -110 °C removes the adsorbed water from the top surface. At this temperature freeze-drying effects are not significant enough to influence the measurements during normal analysis times.

AS-ThP4 Conformational Susceptibilities of Peptides at Interfaces, W.K. Browne, R.L. York, O. Mermut, P.L. Geissler, G.A. Somorjai, University of California at Berkeley

We have used a combination of surface-specific experimental techniques and molecular simulations to examine the adsorption of short chain polypeptides at hydrophilic and hydrophobic interfaces. Sum frequency generation (SFG), a non linear optical spectroscopy, in concert with Monte Carlo simulations provide insight into the effect of adsorption on polypeptide conformation. Since hydrophobic phenomena are known to have a large effect on any peptide system, our simulations include an explicit coarse-grained solvent. Particularly, the structural features of polylysine at the hydrophobic and hydrophilic interface have been examined. In addition, key forces in the adsorptive behavior of poly-lysine are isolated. Using the data from computer simulations and SFG spectra, the structural characteristics of short chain polypeptides at hydrophilic and hydrophobic interfaces will be presented.

AS-ThP5 Investigation of the Use of IR Ellipsometry for the Detection of Biological Molecules, S. Sarkar, University of Nebraska, Sweden

FTIR spectroscopy has been in wide spread use for the detection and identification of the definitive 'fingerprints' of molecules for some time now. Most applications of FTIR spectroscopy have been limited to utilizing and interpreting mostly transmitted and reflected intensities either in terms of relative intensities or as circular dichroism changes. Thin films formed by biological molecules have thus been investigated and limited use of ellipsometric analysis made. The limited use mainly attributable to the limitations of the method as well as the esoteric theory and modeling required in interpreting the results. In our current work, we investigate the use of an attenuated total internal set up to perform IR ellipsometry on a few model biological molecules and present preliminary data obtained there off. Molecules of interest were chiefly human albumin, immunoglobulin and fibrinogen.

AS-ThP6 Surface Potential Imaging of Self-Organized DNAs acquired by Kelvin Probe Microscopy, T. Ishizaki, N. Saito, O. Takai, Nagoya University, Japan

Bioelectronics has been known as a frontier in electronics since biomolecules have attractive functions, which may not be artificially created. Generally, biomolecules work in self-organized units. Novel devices with complex or fuzzy functions would be fabricated when biomolecule is mounted on electronic devices. At first, the basic characteristics of biomolecules on various surfaces must be evaluated toward such technical innovations. There are some reports on the self-organized structures and mechanical properties of biomolecules with atomic force microscopy (AFM) and scanning tunneling microscopy (STM). However, the electric properties have not yet been evaluated by 2-dimensional images, since it is difficult to acquire such images. Kelvin probe force microscope (KPFM) is a powerful tool for measuring microscopic surface potential. In this study, we aim to acquire surface potential images of self-organized DNAs. The DNA sample used in this research was poly(dA-dT)_n. The DNA was dissolved in ultrapure water (18.2 M Ω) or 0.1 mM MgCl₂. The solutions of 10 μ l were dropped onto Si(111) substrate, amino-terminated Si(111) substrate or HOPG. The sample solution was allowed to remain on the substrates for 1min and it was then blown off with air. The surface potential images of the samples were acquired by Kelvin probe force microscopy (KPFM). We first observed that the network structure of DNA was formed. The mean height of DNA was 1.2 nm, indicating that the

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clusters mainly comprised a single layer of DNA molecule. This may be due to an attractive electrostatic force between the substrates and the phosphate group of DNA. The clear surface potential images of self-organized DNA on Si and HOPG were acquired under the condition of an a.c. voltage of 2 V and a frequency of 23 kHz. The surface potential of DNA was c.a. 10 mV higher than that of Si substrate, while it was c.a. 20 mV lower than that of HOPG.

AS-ThP7 Surface Potential Measurement of Human Hair using Kelvin Probe Microscopy, R. Lodge, B. Bhushan, The Ohio State University

Surface charge of human hair has a significant effect on manageability, feel, and appearance. For this reason, controlling charge buildup to improve these factors is an important issue in the commercial hair care industry. In this study the surface potential of human hair is measured using the Kelvin Probe method with an atomic force microscope (AFM). Charge is induced triboelectrically by rubbing lightly with a silicon AFM tip. The potential is then measured with a conductive tip over an area containing the charged surface. Caucasian virgin (undamaged), chemically damaged, and mechanically damaged hair samples are studied to determine the effect of damaging treatments on surface charge properties. Virgin samples of African and Asian subjects were measured to determine if ethnicity dependence exists. Samples treated with commercial conditioner as well as those treated with an amino silicone conditioner are also studied to determine the effect of conditioner treatment. Similarly, the effect of surrounding environment is studied by varying the relative humidity and temperature of the sample during both charging and surface potential measurement. The contrast in electrical properties between cuticle scale edges and cuticle surface is also presented. Electrical, chemical, and mechanical mechanisms for the given results are discussed and recommendations given.

AS-ThP8 Fabrication of Nanoscale Craters In PMMA Due to Exposure to Condensing Solvent Vapor, C.M. Bates, S.C. Langford, J.T. Dickinson, Washington State University

When cooler surfaces are exposed to hot vapors, nucleation of tiny droplets can occur. We exploit this condensation to explore the consequences of exposure of poly(methyl methacrylate) films to formic acid vapor. After rapid evaporation of these droplets we observe the surface with atomic force microscopy. The surface is dramatically modified by the formation of nanometer scale craters. Careful image analysis suggests that the mechanism is a combination of two processes: (a) dissolution and transport of polymer to the rim of the crater, similar to the formation of coffee stain patterns described by Deegan, and (b) densification of the polymer during resolidification. Such features could be useful for modifying the surface properties of the polymer, serve as molecular reservoirs, and possibly modify the mechanical properties of the surface.

AS-ThP9 Surface Characterization for MEH-PPV of Difference Molecular Weight Analyzed by XPS and SPM, N. Keiichi, I. Yoshitoki, O. Toshiyuki, JEOL Ltd., Japan

It is well known that x-ray photoelectron spectroscopy (XPS) is a meaningful analytical technique for the chemical characterization of polymer compounds. In particular, surface segregation occurs by a change of molecular weight in polymer. Recently, the development of organic EL materials advances, and the characteristic of these materials are analyzed by various analysis instruments. Usually, structural analysis of organic EL materials is investigated by GC-MS and NMR. On other hand, XPS is used for surface chemical composition analysis mainly. However, organic EL materials are different in a characteristic by a difference of molecular weight. In particular, EL luminous efficacy of high polymer materials shows molecular weight dependence. In this work, we examined the chemical bonding state and structure of different molecular weight organic EL material. We have investigated MEH-PPV [poly(2-methoxy,5-(2-ethylhexyloxy)-p-phenylenevinylene)] of different molecular weight. This MEH-PPV die formation with THF solvent on ITO film. X-ray photoelectron spectrometer used for this experiment is JPS-9200 (JEOL.Ltd.), and the measurement condition is as follows. X-ray used this measurement is AlK α monochromatic x-ray, and energy resolution for each elements is 0.65 eV. The surface was observed with SPM (JSPM-5400, JEOL Ltd.). The next results were provided from XPS measurement. It was observed that the amount of C-O group decreased with increase of molecular weight, and CH peak intensity and FWHM of CH peak increased. After decrease of surface segregation, as for the increase of CH peak intensity and FWHM, recombination of hole and electron occurs in CH intramolecule.

AS-ThP10 Application of a Recent Algorithm to Patterned Polymer Overlayers, S. Hajati, S. Tougaard, University of Southern Denmark; J.J. Coultas, C. Blomfield, Kratos Analytical Ltd, UK

Initial studies have shown the potential of a recent algorithm¹ for the processing of XPS image data.² The algorithm lends itself to automated data processing, essential for the practical analysis of XPS images. Application of the algorithm determines both the total amount of atoms within the outmost 3 inelastic mean free paths and an estimation of their depth distribution. In this work we extend the application of the algorithm to a series of samples with overlayers of known thicknesses to produce a more accurate indication of the depth distribution. The resultant images show both the amount and depth distribution of each element. We also look at ways of streamlining the data acquisition to develop this in to a practical technique for producing thickness maps. ¹S. Tougaard, J. Vac. Sci. Technol. A21, 1081 (2003) ²S. Hajati, S. Coultas, C. Blomfield, S. Tougaard, Surf. Sci. (2006).

AS-ThP12 Applications of ToF-SIMS in a Research and Development Laboratory, V.S. Smentkowski, S.G. Ostrowski, GE-GRC-N

Time of flight secondary ion mass spectrometry (ToF-SIMS) has a number of desirable characteristics for surface analysis in a research and development laboratory. In this presentation, we show the benefits of ToF-SIMS analysis via real industrial examples. We will show that ToF-SIMS is able to detect and image species that are below the detection limit for other analytical instruments. We will also show that depth profiles measured on ToF-SIMS instruments are comparable to depth profiles measured on dynamic SIMS instruments. One advantage of performing depth profiles using ToF-SIMS instrumentation is that an entire mass spectrum is saved at each depth and the analyst can perform retrospective analysis and/or multivariate statistical analysis of the entire measured depth profile data set in order to understand the material. In a research and development laboratory, the analyst does not always know a-priori which species should be monitored; we will show that advanced multivariate statistical analysis tools are useful for a complete analysis of the measured data.

AS-ThP15 Doping Area Analysis using Atomic Force Microscopy in Si Devices, K.-W. Kim, E.-J. An, K.-Y. Choi, S.-Y. Lee, Hynix Semiconductor Inc., Korea

In the fabrication of nano-scale silicon devices, accurate doping area characterization is one of the important fields to be solved. Characterization methods such as scanning capacitance microscopy (SCM) and scanning spreading resistance microscopy (SSRM) have provided two-dimensional profiling of the carrier distribution in semiconductors. In this study, the possibility and the effectiveness of applying the atomic force microscopy (AFM)-imaging combined with delineation method are discussed for two-dimensional dopant profiling. Shallow junctions were fabricated in p-type silicon wafers by the implantation of As ions (~10¹⁵/cm²) at an energy of 55keV. Also selective etching was successfully performed using the chemical etching solutions of HF:HNO₃:CH₃COOH mixture. We found that different etching rates of the doped regions resulted in a surface topography, height difference and surface roughness. The reason for the visibility of dopant distribution is the relatively strong changes of the etching rate and the stained surface roughness in dependence on the doping concentration. We focused on evaluating an adequate roughness, etch line profile and the junction depth position in the junction area. The resulting dopant profile shapes and junction depth resembled the ones as measured by secondary ion mass spectroscopy (1-D), transmission electron microscopy combined with delineation and SCM (2-D). The spatial resolution of the chemical delineation was extremely good (better than 10nm) due to the capabilities of the AFM-microscope. Especially, dopant depth profiles of arsenic showed the similar values of junction depth (~200nm) at the above methods for a medium dose range. Further investigations are required that the accuracy of the measurement is determined by the repeatability of the etching procedure and the dopant concentration is related to the delineated surface roughness quantitatively.

AS-ThP16 Stress in FIB Exposed Si, K.M. Archuleta, D.P. Adams, M.J. Vasile, Sandia National Labs; J.E. Fulghum, University of New Mexico; P.G. Kotula, Sandia National Labs

Focused Ion Beam (FIB) systems are increasingly utilized for the milling of micro-tools and building of architectures on the nano-scale. It is thus critical to understand the impact of FIB milling on the properties of relevant materials. In this study, high energy (30 keV) focused gallium ion beams are

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used to expose silicon samples. The samples are then removed and analyzed using ex-situ techniques. Compressive stress due to FIB shaping of silicon is investigated through atomic force microscopy (AFM), optical interferometry, tunneling electron microscopy (TEM) and x-ray photoelectron spectroscopy (XPS) measurements.

AS-ThP17 Quantification of Fe-Ni Alloy Films by XPS, AES and SIMS. *K.J. Kim*, Korea Research Institute of Standards and Science, Republic of Korea; *D.W. Moon*, Korea Research Institute of Standards and Science, Korea; *C.J. Park*, *H.J. Song*, Korea Research Institute of Standards and Science; *D. Simons*, *G. Gillen*, National Institute of Standards and Technology; *H. Jin*, *H.J. Kang*, Chungbuk National University, Korea

Although XPS and AES are commonly used for the quantitative surface analysis of multi-component materials, quantitative analysis of alloy and compound materials is still difficult because of both the matrix effect occurring in quantification and the surface composition change by ion beam sputtering. Therefore, we need reference materials to ensure reliable analysis. It is more desirable that reference materials should minimize both the matrix effect and the surface composition change during ion sputtering for surface cleaning. Quantification of Fe-Ni alloy thin films was suggested as a new subject for a pilot study in the surface analysis working group of CCQM. Fe-Ni alloy thin films have been developed as the certified reference materials (CRM) for quantitative surface analysis by XPS and AES. Fe-Ni alloy films (Fe28 at%-Ni 72 at%, Fe51 at%-Ni 49 at%, Fe78 at%-Ni 22 at%) were grown on Si (100) wafers by ion beam sputter deposition. The relative compositions of the alloy films were controlled using in-situ XPS analysis. The nominal compositions of the CRMs were certified by inductively coupled plasma-mass spectrometry with the isotope dilution method. SIMS depth profiling using a C₆₀⁺ ion source showed uniform depth distributions of relative compositions. The Fe concentrations of the three specimens selected from the center, medium and edge of the 6 inch wafer showed a good agreement within the relative standard deviation of 0.05 %. In this study, some preliminary results for the CCQM pilot study will be presented. The quantification of Fe-Ni alloy films was performed by XPS, AES and SIMS. Sputtering of Fe-Ni alloy films with 0.5 - 5 keV Ar ions showed no severe modification in surface compositions. For nominal surface composition and measured composition, the calibration curves of the alloy compositions by XPS, AES and SIMS showed almost identical slopes within the range of 1.01 - 1.03.

AS-ThP18 Epitaxial Growth of NbN and MgO Films for Superconducting Single Photon Detectors and Josephson Junction Qubits. *J.S. Kline*, *S. Oh*, *R.H. Hadfield*, *A. Lita*, *S.W. Nam*, *D.P. Pappas*, National Institute of Standards and Technology

The growth of ultrathin epitaxial aluminum oxide tunnel barriers on Re has been proven to reduce the number of spurious resonators in Josephson phase qubits when compared to qubits fabricated with amorphous tunnel barriers. Other epitaxial tunnel barrier materials such as MgO may also improve device performance. The superconductor NbN is latticed matched to MgO and was studied in this work. The NbN/MgO material system is also well suited for superconducting single photon detectors and NbN thin films were grown for this purpose. Niobium nitride films were deposited on MgO substrates by UHV reactive sputtering in an argon/nitrogen gas mixture. Magnesium oxide tunnel barriers were deposited by RF sputtering and also by reactive evaporation of magnesium in a controlled oxygen background. To achieve epitaxy, the substrate was held at elevated temperature during the deposition. Surface science tools such as Auger electron spectroscopy, scanning tunneling microscopy, and reflection high energy electron diffraction were used for in-situ analysis of the grown films.

AS-ThP19 Large-Area Pulsed-Laser-Deposition of Dielectric and Ferroelectric Thin Films. *S. Sakai*, *M. Takahashi*, *K. Motohashi*, *Y. Yamaguchi*, *N. Yui*, *T. Kobayashi*, National Institute of Advanced Industrial Science and Technology, Japan

Pulsed laser deposition (PLD) is a successful method for obtaining high quality films of various kinds of materials, and has an advantage of clean deposition without impurities of undesired element (e.g., carbon) in the films. However, the PLD method tends to show poor uniformity of film thickness mainly due to small laser-ablation plume, thus PLD has not been regarded as a good method for large-area thin-film depositions. In order to improve the thickness uniformity, we recently developed the PLD technology using a prototype machine of VPLD-8000 (Vacuum Products Co Ltd) and succeeded in depositing large-area films of high-k dielectric HfO₂ and ferroelectric SrBi₂Ta₂O₉ (SBT) on Si wafers. In this work, we demonstrate good thickness uniformity of 8 and 6inch HfO₂ and 4inch SBT films. The HfO₂ was deposited at

room temperature in 13Pa N₂. The SBT was deposited at 400°C in 13Pa O₂. Standard deviations of the thicknesses all over the 42nm-thick 8inch HfO₂, 6nm-thick 6inch HfO₂, and 94nm-thick 4inch SBT were 1.3%, 1.6%, and 1.2%, respectively. Cross-sectional TEM showed that an interfacial layer between HfO₂ and Si was thinner than 1nm in the 6nm-thick 6inch HfO₂. Standard deviation of accumulation-mode capacitances was 1.9% for Pt/HfO₂/Si MIS diodes, which were fabricated by evaporating Pt top electrodes on a diametrical line of the 6nm-thick 6inch HfO₂ and annealing at 700°C in N₂ for 10 min. In our PLD technique, KrF laser beam is aligned parallel to a face-down substrate surface, and a 3x12cm² ceramic target is set to be inclined to the substrate surface by 30°. Since the substrate does not block off the incident laser beam, available Si wafer size is easily extendable to 300mm in diameter. Therefore, our developed PLD technique meets industrial needs of high and uniform qualities over large area of high-k dielectric and/or ferroelectric thin films for LSIs.

AS-ThP20 Ordered Au(111) Surfaces Grown on Si(111). *K. Pedersen*, *A. Silva*, Aalborg University, Denmark; *P. Morgen*, University of Southern Denmark, Denmark; *Z.S. Li*, University of Aarhus, Denmark

Gold surfaces are the primary choice as substrate in studies of organic structures on surfaces since they are stable in various biochemical environments and allow attachment of biomolecules through thiol groups. Typically, surfaces of bulk Au crystals or thin films on Mica are used. However, formation of well-ordered thin Au films on Si would be a step in the direction of direct integration of biosensors on wafers containing Si electronics. Deposition of Au directly on Si leads to formation of a disordered surface layer containing a mixture of Si and Au that floats on top of the Au layer even for relatively thick Au films. In the present work the properties of thin Au films grown on top of a thin (7 layers) Cu film as a buffer between the Si substrate and the Au overlayer are described on the basis of photoemission spectroscopy and AFM. Previous investigations have shown that the Cu buffer layer improves the growth of Ag and Al relative to direct growth on clean Si(111)7x7. For both Ag and Al the Cu buffer layer leads to improved sharpness of quantum well (QW) peaks and surface states. The present experiments demonstrate that also in the case of Au deposition a thin Cu layer improves the film properties. A sharp Au(111) LEED pattern is observed even for films that are only a few layers thick. The Shockley surface state characteristic of Au(111) surfaces appears at a binding energy of 0.5 eV. Furthermore, structures appear that disperses toward the sp-band edge 1.1 eV below the Fermi level as the film thickness grows. This is characteristic of QW levels. The energy window for observing QW effects is narrow in Au compared to for instance Ag and Al where the sp bands extend over ~4 eV. In Au the window from the sp-band edge to the onset of the d-bands is less than 1 eV. The appearance of QW levels indicates flat domains on the atomic monolayer level. This is supported by AFM and STM investigations performed ex situ on the samples investigated by photoemission.

AS-ThP21 Aluminum Induced Crystallization (AIC) of Amorphous Silicon. *H.M. Meyer*, Oak Ridge National Laboratory; *K. Sharif*, *H. Naseem*, *H.H. Abu-Safe*, *W.D. Brown*, University of Arkansas

A process for producing epitaxial Si thin films using the method of aluminum induced crystallization (AIC) of amorphous silicon (a-Si) was investigated. AIC holds promise for producing polycrystalline Si (p-Si) on inexpensive glass and plastic substrates. TEM and Auger analysis have shown that these efforts were successful. Initial results from Auger depth profiles showed that while we achieved a good measure of the composition versus depth, reproducing the data was difficult, even from a small area on the same sample. The complexity of these systems was revealed by interrupting the depth profiles and mapping the lateral distribution of Si, Al, and O. These 2-D maps readily showed that the distribution was more complex than anticipated. A second set of samples, prepared to bracket the optimum AIC anneal time for a given temperature, was analyzed by Auger microanalysis to further explore the nature of the Al/Si intermixing. All of the samples for this group were prepared by depositing a 300 nm Al layer onto the Si wafer, followed by a 300 nm layer of a-Si. This poster will present results for samples annealed at 525°C for times ranging from 0 min to 120 min. Auger elemental maps of a cross-section for a sample no annealing showed individual layers, with a-Si on top. Depth profiles for annealed samples clearly show changes occurring on the surface after 10 min of annealing and that further annealing drives the AIC process. Research sponsored by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of FreedomCAR and Vehicle Technologies, as part of the High Temperature Materials Laboratory User Program, Oak

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Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract number DE-AC05-00OR22725.

AS-ThP22 MD/MC Simulations of Reactive Sputtering Deposition of Amorphous SiO₂, M. Taguchi, S. Hamaguchi, Osaka University, Japan

Silicon Dioxide (SiO₂) thin film deposition processes were studied with the use of classical Molecular Dynamics (MD) simulations combined with Monte Carlo (MC) simulations. The effects of the incident energy and angle of deposition species on film properties and high energetic argon ions during reactive sputtering deposition processes for amorphous SiO₂ are examined. From the simulation results, it has been confirmed that some properties of the deposited film strongly depend on the incident energy and angle of Si atoms sputtered from the target. For example, the film density is shown to become lower at lower Si incident energy and larger Si incident angles. The stoichiometry of the film expressed by the ratio of the number of O atoms to that of Si atoms contained in the film has been also shown to increase as the Si incident energy decreases and Si incident angle increases. In other words, as the vertical momentum of Si atoms becomes small, the film becomes more oxygen rich and porous. Possible physical mechanisms causing these effects are also discussed from the viewpoint of motion of incident Si atoms interacting with the surface atoms. It is also confirmed that additional injections of highly energetic argon ions further press the SiO₂ thin films to make them denser. If the argon incident kinetic energy is sufficiently high, however, etching of the deposited films also takes place.

AS-ThP23 Development of Closed Field Reactive Magnetron Sputtering for Multilayer Optical Coating, J.M. Walls, D.R. Gibson, E.M. Waddell, Applied Multilayers Ltd, UK

Closed Field reactive magnetron sputtering has been used for many years to produce state-of-the-art tribological and wear resistant coatings. In this paper, we report on its recent development and application to multilayer optical coatings. Optical coatings require precise control of the stoichiometry of dielectric metal oxides and layer thickness control within sub-nanometre tolerance. The process operates with metal targets and although the targets are partially oxidised the deposition rates are close to the metal mode. This requires the use of pulsed dc power and a new hysteresis control strategy based on monitoring target Voltage. Thickness control is achieved using time only. In addition, the process incorporates shutters to allow target pre-conditioning and fine interface control. In addition to describing the new process, this paper will discuss the optical properties of a range of optical materials including dielectrics such as SiO₂, Nb₂O₅, TiO₂, ZrO₂ and Al₂O₃ together with important transparent conducting oxides such as indium tin oxide (ITO). The Closed Field technique produces reactive plasma conditions that combine low energy (5mA.cm⁻²) to provide ideal conditions for thin film growth with the further advantage that the vacuum hardware is relatively simple and there is no requirement for an auxiliary ion or plasma source. The process produces non-absorbing, dense, spectrally stable coatings that are also exceptionally smooth (rms roughness typically

AS-ThP24 Advanced Process Modelling of the Rotating Magnetron, O. Kappertz, T. Kubart, T. Nyberg, S. Berg, Uppsala University, Sweden

Thin films of transition metal oxides and nitrides find numerous applications in modern technology, for example as antireflective or protective coatings in architectural glazings. Frequently such films are deposited by direct current reactive magnetron sputtering, and for large area coatings rotatable magnetron systems are commonly used. The rotation of a cylindrical target around a fixed magnet system leads to a uniform target erosion, and thereby more efficient material utilization and extended target lifetime. In such a setup a fixed point at the target surface is periodically exposed to sputter erosion, while for the rest of the period compound is formed at the target surface due to its exposure to the reactive gas. Recently a simplified analytical model has been proposed, which describes how several parameters, like the speed of the target rotation, size of the sputter zone and the current density, influence the compositional balance between compound formation and removal. In this report, the model is extended by including a full numerical simulation of the dynamical balance between sputter erosion and compound formation by both chemisorption and ion implantation. The influence of the target rotation on processing characteristics is discussed and compared to experimental observations.

AS-ThP26 Decomposition of Titanium Deuteride Films Protected by Ultra-Thin Pd Layers; Thermal Desorption Kinetics Studies Combined with Microstructure Analysis of Bimetallic Films, W. Lisowski, Polish Academy of Sciences, Poland; E.G. Keim, University of Twente, The Netherlands, Netherlands; A.H.J. van den Berg, M.A. Smithers, University of Twente, The Netherlands; Z. Kaszukur, Polish Academy of Sciences, Poland

Thin titanium films can be applied as hydrogen storage material due to titanium hydride formation. Exposing hydrated Ti films to ambient conditions leads however, to a partial decomposition of titanium hydride. This can be prevented by covering such films by Pd. Here we present the results of TDMS, XRD, SEM, TEM and XPS, dealing with the question as to how TDMS controlled decomposition of titanium deuteride (TiD@sub y@) from films protected by Pd proceeds, and how TDMS heating affects the interface and bulk structure of such bimetallic films. TiD@sub y@ films were prepared in UHV conditions at 300 K by exposing 100 nm thick Ti films to D@sub 2@. The TiD@sub y@ phase formation which results from this volumetrically controlled adsorption procedure, previously detected by ToF-SIMS, was now confirmed by XRD. The TiD@sub y@ film was subsequently covered in-situ by a 6-20 nm thick Pd layer. Desorption of D@sub 2@ was monitored in situ by TDMS (see Ref. 4 for a description), all other analyses ex situ. It was found that a Pd layer, protecting the TiD@sub y@ films, only slightly changes the thermal desorption kinetics of D@sub 2@ from the TiD@sub y@ films. Thermal decomposition of TiD@sub y@ is accompanied by a structural transformation of TiD@sub y@ into an α -Ti phase, resulting in less plastically deformed Pd/Ti films. However, we observed also TDMS heating induced intermixing of Pd and Ti phases within the Pd/Ti interface. Complex structures, including Moiré patterns, have been identified. W. Lisowski, A.H.J. van den Berg, M.A. Smithers (1998) Surf. Interface Anal. 26, 213 (1998). W. Lisowski, E.G. Keim, A.H.J. van den Berg, M.A. Smithers, Anal. Bioanal. Chem., in press. W. Lisowski, A.H.J. van den Berg, D. Leonard, H.J. Mathieu, Surf. Interface anal. 29, 292 (2000). W. Lisowski, E.G. Keim and M.A. Smithers, J. Vac. Sci. Technol. A21, 545 (2003).

AS-ThP27 Photocatalytic Decomposition of CH₃OH on TiO₂ Sputter Films Prepared by Changing Ar/O₂ Ratio and Working Gas Pressure, T. Takahashi, K. Prabakar, University of Toyama, Japan; T. Nakashima, Kashiwa Chuo High School, Japan; Y. Kubota, University of Yokohama City, Japan; A. Fujishima, Kanagawa Academy of Science and Technology, Japan

TiO₂ has attracted considerable attention as a photocatalyst with strong activity. We found that TiO₂ sputtered films prepared under heavy plasma exposure exhibited good photocatalytic decomposition of CH₃OH. However, the TiO₂ films showed less than perfect transparency because of the slightly opaque surface. For practical use, transparency is desirable. In this study, to deposit transparent TiO₂ films, the substrates were placed at a position removed from the plasma. TiO₂ films were deposited on glass slide substrates. The ratio of Ar to O₂ (G@sub R@) were 9:1, 8:2, 7:3 and 6:4. The crystallographic and surface structures and optical properties of TiO₂ films deposited at working gas pressures (P@sub W@) ranging from 0.2 to 0.8 Pa were investigated in detail. The decomposition of gaseous methyl alcohol was performed to investigate the dependence of the photocatalytic reactions on the structures and properties of the TiO₂ films. In all of the TiO₂ films, only the A(101) diffraction peak was observed from the x-ray patterns, where A indicates anatase TiO₂. The crystallinity improved greatly with decreasing P@sub W@. The transmittances of all of the TiO₂ films were constant at 80-90 % for wavelengths in the range of 900 nm to 380 nm. The as-deposited TiO₂ films successfully photocatalyzed the decomposition reaction of CH₃OH to CO and H₂O, according to the infrared transmittance spectra. The decomposition rate using the TiO₂ films increased with increasing P@sub W@. For the TiO₂ films deposited at a P@sub W@ value of 0.8 Pa and a G@sub R@ value of 2.3, the CO formation rates were about 2.2 times higher than those prepared at a G@sub R@ value of 9 for a solar irradiation time of 130 min. In conclusion, the transparent TiO₂ films deposited in this study are quite photocatalytically active, supporting the decomposition of gaseous methyl alcohol.

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AS-ThP28 A Short Review on the ESSCR Mechanism for Phosphor Degradation, H.C. Swart, J.J. Terblans, E. Coetsee, O.M. Ntwaeaborwa, M.S. Dhlamini, University of the Free State, South Africa; P.H. Holloway, University of Florida

Standard cathodoluminescent phosphors normally lose brightness upon bombardment with electron beams. A combination of techniques such as XPS (X-ray photoelectron spectroscopy), AES (Auger electron spectroscopy) and CL (cathodoluminescence) was used to show that the main reason for the degradation in CL intensity is the formation of a non-luminescent dead layer on the surface due to a electron stimulated surface chemical reaction (ESSCR). The decrease in luminance was found to be a result of the growth of the dead layer. Different phosphors which include sulphide-based as well as oxide-based phosphors reacted similar under electron bombardment. When ZnS phosphor powder was exposed to the electron beam in a water-rich O@sub 2@ ambient, a chemically-limited ZnO layer was formed on the surface. A layer of ZnSO@sub 4@ was formed on the surface during the electron beam degradation of the ZnS phosphor powder in a dry O@sub 2@ ambient. The electron stimulated reaction led to the formation of a luminescent SiO@sub 2@ layer on the surface of the Y@sub 2@SiO@sub 5@:Ce phosphor powder. CeO@sub 2@ and CeH@sub 3@ were also detected on the surface. An increase in the CL intensity at a wavelength of 650 nm was measured during the formation of the luminescent SiO@sub 2@ layer. A less effective SiO@sub x@ (0<x<2) matrix layer was the main cause of degradation of the CL intensity of SiO@sub 2@:Ce,Tb nano-phosphor as well as SiO@sub 2@:PbS nano-phosphor.

AS-ThP29 Synthesis and Characterization of Erbium Doped Metal Oxide Nanofibers for Applications in Thermophotovoltaics, E.T. Bender, R. Wang, M.T. Aljarrah, E.A. Evans, R.D. Ramsier, The University of Akron

We report on the synthesis, characterization, and near-infrared emission of erbium doped metal oxide nanofibers, for applications in thermophotovoltaics (TPV). Erbium emits radiation selectively in the 6000 to 7000 wavenumber region, which can be converted into electricity by appropriately chosen photocells. Thus, TPV technology enables the direct conversion of thermal energy to electrical energy, with no moving parts. Erbium can be used as a coating on a solid substrate such as metal or ceramic. However, the greybody radiation from the substrate will reduce the overall efficiency of the TPV system, and can lead to excessive heating in the photocell. We overcome this problem by doping metal oxide nanofibers, typically titania, with erbium via an electrospinning process. These doped fibers are characterized with scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), X-ray fluorescence (XRF) and Fourier transform infrared spectroscopy (FTIR). The structure of the doped nanofiber mats is ideally suited for direct heating in gas-flow applications, such as exhaust systems. Near-IR emission measurements are carried out using a quartz tube, with the self supporting nanofibers heated by the exhaust from a propane flame. We therefore demonstrate the ability of these nanofibers to function in TPV gas flow applications.

AS-ThP30 Complimentary Information from Auger and EDS Analyses of Particles and Thin Films, S.A. Wight, NIST

Auger electron spectroscopy (AES) and x-ray spectrometry are complementary: both are the result of a primary electron beam interacting inelastically with specimen atom core electrons. A core electron is ejected and as a higher level electron moves to fill the vacancy, the energy difference between these levels is released either with the ejection of another bound outer shell electron as an Auger electron with a characteristic kinetic energy or as a characteristic x-ray photon. Auger electrons and x-rays are produced throughout a sample volume defined by the beam energy and specimen composition, but the sampling depths are quite different. While x-rays can suffer absorption, those that escape retain their characteristic energy and therefore represent the entire range of generation, which may be micrometers. Because of the simultaneous nature of energy dispersive x-ray data collection, the entire spectrum can be collected at each pixel and post processed for composition. Auger electrons suffer inelastic scattering and so can only travel a small distance in the sample while retaining their characteristic energy. Only the Auger electrons that are created within a few nanometers of the surface have a sufficient mean free path to escape the specimen and be collected for analysis. Auger electrons are measured with a spectrometer that has a narrow energy bandpass and must be sequentially scanned to record the spectral energy range of interest. Auger spectroscopy provides elemental and chemical information because the atomic energy levels involved in Auger emission are also influenced by chemical bonding between atoms. The complementary nature of Auger and x-ray microanalysis with their

different sampling depths can be exploited to view the composition of the bulk and the surface of a specimen.

AS-ThP31 Atom Probe Characterization of Thin Films, D.J. Larson, Imago Scientific Instruments Corp

To accelerate research and development cycles for devices dependant on nanoscale materials, it is important to correlate device microstructure with specific processing conditions and physical properties. In the magnetic storage and semiconductor industries, this is particularly important due to the ever-shrinking characteristic length scales on which devices are being fabricated. Atom probe tomography@footnote 2,3@ has the capability to play an important role in this development due to its capability to provide quantitative 3-D atomic-scale imaging together with high analytical sensitivity. Local electrode atom probe (LEAP®) technology combines sub-nanometer spatial resolution with chemical composition at scales on the same order as device structures. In this presentation, applications of the LEAP microscope to a variety of nanomaterials systems used in the magnetic recording and semiconductor industries will be presented. These systems include 1) magnetoresistive spin valves and tunnel junctions@footnote 5,6@ which are two structures commonly used to form the "reader" portion of magnetic recording heads, 2) current-confined-path spin valve structures 3) perpendicular recording media in which oxygen is used to isolate magnetically the individual grains in Co-based alloys, 4) ultra shallow dopants implanted in silicon, and 5) silicon-germanium (SiGe) layered structures. @FootnoteText@ @footnote 1@ R. L. Comstock, J. Mat. Sci. Mat. Elec. 13(9) (2002) 509. @footnote 2@ A. Cerezo et al., Rev. Sci. Instrum. 69 (1998) 49. @footnote 3@ M. K. Miller, Atom Probe Tomography, Kluwer Academic Publishers, New York, 2000. @footnote 4@ T. F. Kelly et al., Micro. Microanal. 10(3) (2004) 373. @footnote 5@ D. J. Larson, Thin Solid Films 505 (2006) 16. @footnote 6@ D. J. Larson et al., Acta Mater. 52(10) (2004) 2847.

AS-ThP32 Relative Sputter Rates of Oxide Films: Constancy, Energy and Angle Dependence, A.S. Lea, M.H. Engelhard, D.R. Baer, T. Droubay, P. Nachimuthu, Pacific Northwest National Laboratory

The increased use of oxide films for a variety of applications has produced a significant interest in knowing the relative rates that different oxides sputter. Because of the wide use of oxide films in our laboratory we have undertaken a series of measurements comparing the relative rates of sputtering of a variety of thin film oxides to a known thickness of SiO@sub 2@ on Si. We have found that these sputter rates differ by more than a factor of two. It is well established for pure materials that the sputter rates significantly change extensively as a function of energy and angle. In addition to the influence of damage that can also alter sputter rates, oxides may be susceptible to various stages of disorder and ion beam induced reduction that may lead to depth dependent changes in sputter rate. In this paper we report a series of measurements to determine the constancy of the oxide sputter rates and the dependence of the relative rates on angle and energy. We are using a number of different oxide films of known thickness, including @alpha@-Cr@sub 2@O@sub 3@, anatase, rutile, and zinc oxide. The oxides have been grown by MBE or PLD and measured by XRR. Time dependent sputter rates are being measured by EDS using a method described by Musket and Strausser. @footnote 1@ The energy and angle dependences are being made by argon ion sputtering in a Phi Quantum 2000 XPS system or a Phi 680 Auger Nanoprobe system that contains an EDS analyzer. @FootnoteText@ @footnote 1@ RG Musket and YE Strausser, Appl. Phys. Lett 37 (1980) 478-480.

AS-ThP33 Transient Effects during Cs/Ga Dual Beam TOF-SIMS Profiling: Experiment and Simulation, R.G. Vitchev, J. Brison, L. Houssiau, Facultes Universitaires Notre-Dame de la Paix, Belgium

Cs@super +@ sputtering beams are widely used in TOF-SIMS dual beam depth profiling. Loading the surface with Cs increases the negative ion yields and leads to formation of MCs@super +@ secondary ions (M stands for matrix). It was shown that the MCs@super +@ ions are suitable for quantitative analysis since they are relatively insensitive to matrix effects. Secondary ion yields change dramatically in the initial stage of the Cs bombardment due to the increase of the amount of implanted Cs in the surface until a steady-state is reached. This could be a problem if ultra-thin (nm) layers are analyzed. Having a better understanding of these transient phenomena is therefore crucial for such applications. In this work the secondary ion emission from Si H-terminated surface sputtered by Cs@super +@ ions (250 eV - 1 keV, 45°) and analyzed by 15 keV Ga@super +@ ions was studied. Xe@super +@ (350 eV) sputtering was used to determine the depth profile of the implanted Cs at steady-state. The steady-state Cs surface concentration was measured by XPS. A dynamic

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TRIM code was used to simulate the sputtering and composition change of the Si target under Cs bombardment and obtain the energy/velocity distribution of the atoms sputtered by the analyzing Ga beam. These results, combined with the electron tunnelling model for ion formation, were used to calculate the secondary ion yield at different Cs doses. The results were compared to those obtained experimentally.

AS-ThP34 Preliminary Report of Evaluation of Automated Peak Detection Procedure in X-ray Photoelectron Spectra, M. Suzuki, ULVAC-PHI, Inc., Japan; *S. Fukushima, S. Tanuma,* NIMS, Japan

X-ray photoelectron spectra should be analyzed to detect peaks prior to elemental/chemical assignment and the peak detection routine has been discussed in ISO/TC201/SC3 activity. It is needed to estimate its effectiveness of the software as well as the uncertainties of the results and it has been investigated in VAMAS activity. Prior to the world-wide interlaboratory study, the preliminary investigation was performed to make artificial spectral data and analyze their efficiency using a peak detection software routine that included the three algorithms with (1) second derivative method, (2) peak-to-background method, and (3) background estimation method. Test spectra were composed from the actually measured Au, Ag, and Cu spectra and the artificially noise-superposed spectra were also composed. The number of the basic spectra is three for the mixing ratio of (Au, Ag, Cu) as (1, 1, 1), (1, 0.1, 0.01), and (1, 0.01, 0.001). The noise-superposed spectra have been prepared for each basic spectrum, considering the noise level and the randomization for each noise level. These basic and noise-superposed spectra were analyzed for peak detection using the software built according to the algorithms above mentioned. The number of detected peaks and the efficiency that is the relative number against the detection number by eyes have been compared for the three basic spectra. The quality of (1, 1, 1) is shown to be different from the other two spectra of (1, 0.1, 0.01), and (1, 0.01, 0.001). For the spectrum of (1, 1, 1) the second derivative method gave a large number of detected peaks than the others. On the other hand, for the spectra of (1, 0.1, 0.01), and (1, 0.01, 0.001) the background method gave a greater number of peaks than the other methods. The number of detected peaks for the noise-superposed spectra drastically decreased from those for the basic test spectra. Detailed results and investigations will be presented and discussed at the conference site.

AS-ThP35 Calculations of Electron Inelastic Mean Free Paths In 12 Organic Compounds and 15 Inorganic Compounds Over the 50 - 30,000 eV Energy Range, S. Tanuma, National Institute for Materials Science (NIMS), Japan; *C.J. Powell, D.R. Penn,* National Institute of Standards and Technology

We have calculated electron inelastic mean free paths (IMFPs) for 50-30,000 eV electrons in 12 organic compounds (26-n-paraffin, adenine, beta-carotene, diphenyl-hexatriene, guanine, kapton, polyacetylene, poly(butene-1-sulfone), polyethylene, polymethylmethacrylate, polystyrene, and poly(2-vinylpyridine)) and 15 inorganic compounds (Al@sub 2@O@sub 3@, GaAs, GaP, H@sub 2@O, InAs, InP, InSb, KBr, KCl, LiF, MgO, NaCl, SiC, SiO@sub 2@, and ZnS)) using their energy-loss functions and the Penn algorithm. The new IMFPs were calculated at equal energy intervals on a logarithmic scale corresponding to increments of 10 %. These IMFPs could be fitted to the modified Bethe equation for inelastic scattering of electrons in matter for energies from 50 eV to 30,000 eV. The average RMS deviations in these fits were 0.12 % for the 12 organic compounds and 0.62% for the 15 inorganic compounds. These RMS values are almost the same as those found in our fits of IMFPs calculated previously for the 50 - 2000 eV energy range. The new IMFPs were also compared with IMFPs from the TPP-2M equation; the average RMS deviations were 8.1 % for the 12 organic compounds and 18.2 % for the 15 inorganic compounds in the 50 eV to 30,000 eV energy range. These RMS value are almost the same as those found (8.5% for inorganic and 19.1% for inorganic compounds) in similar comparisons for the 50 - 2000 eV energy range. Relatively large RMS deviations were found for LiF (47 %), GaAs (37 %), and InAs (26 %). We conclude that the TPP-2M equation is useful for IMFP estimation in other compounds for energies up to 30,000 eV with an average uncertainty of about 18 %.

AS-ThP36 Electron Energy Loss Function for Ultra-Thin HfO₂, Al₂O₃ and Hf-Al-O Dielectric Films on Si(100), H. Jin, S.K. Oh, H.J. Kang, Chungbuk National University, Korea; *S. Tougaard,* University of Southern Denmark

Due to the continuous decrease in device size toward atomic dimensions, Si devices are approaching fundamental limits. To avoid quantum tunneling, high-k (high dielectric constant) gate dielectric layer is required to replace SiO₂. Hf-based transition metal dielectrics have received considerable attention. In particular, high-k alloys, such as aluminate or silicate are

proposed as promising gate dielectrics. Quantitative analysis of reflection electron-energy-loss spectra for ultrathin HfO₂, Al₂O₃ and Hf-Al-O dielectric thin films on Si(100) were carried out by using Tougaard Yubero QUEELS- $\hat{\mu}(k, \hat{\nu})$ -REELS package. For HfO₂, the energy loss function shows peaks in the vicinity of 10, 17, 27, 37 and 47 eV. For Al₂O₃, a broad peak at 22 eV with a shoulder at 14 eV and a very mild shoulder at 32 eV were observed, while for the Al₂O₃ doped HfO₂, the peak position is similar to that of HfO₂. This indicates that when Hf-Al-O film is used as a gate dielectric in CMOS transistor, its electronic structure is mainly determined by the d state of Hf. The results of a quantitative analysis successfully reproduced the trend that has been found in the experimental measurements. In addition, the inelastic mean free path (IMFP) was also calculated from the theoretical inelastic scattering cross-section. The IMFP at 300 eV was about 7.05, 9.62 and 8.48 Å. and that at 500 eV was 11.42, 15.40 and 13.64 Å. for HfO₂, Al₂O₃, Hf-Al-O, respectively.

Applied Surface Science

Room 2005 - Session AS-FrM

Thin Film Characterization

Moderator: S.E. Asher, National Renewable Energy Laboratory

8:00am **AS-FrM1 Probing Interactions of Ge with Chemical and Thermal SiO₂ to Understand Selective Growth of Ge on Si during Molecular Beam Epitaxy**, Q. Li, University of New Mexico; J.L. Krauss, University of Wisconsin Madison; S. Hersee, S.M. Han, University of New Mexico

We have previously demonstrated that Ge selectively grows on Si over a SiO₂ mask during molecular beam epitaxy. We have also demonstrated that epitaxial Ge rings selectively form at the contact region between chemical-oxide-covered Si and self-assembled SiO₂ sphere. In order to determine the surface phenomena responsible for the selectivity, we probed the interactions of Ge with 1.2-nm-thick chemical SiO₂ films and 6 to 200-nm-thick dry thermal SiO₂ films grown on Si(100). The change in Si2p x-ray photoelectron intensity and position, intermittently measured during the Ge beam exposure, reveals that the chemical oxide degrades at substrate temperatures near 600°C. In contrast, the change in thickness and surface roughness of the thermal oxide, measured by ellipsometry and atomic force microscopy, is below the detection limit after a prolonged Ge exposure at temperatures below 700°C. For thermal SiO₂, where oxide degradation is not observed, we have determined that the selectivity stems from the low desorption activation energy (E_{des}) of Ge adspecies from the thermal SiO₂ surface. The experimentally measured E_{des} is 42 ± 3 kJ/mol. The low E_{des} entails a low activation barrier (~ 13 kJ/mol) for surface diffusion. We expect the large diffusion length on the order of 1 μ m to cause Ge adspecies to migrate over SiO₂ and preferentially aggregate on exposed Si surface. In order to determine the identity of stable Ge adspecies on SiO₂, the nucleation of Ge on thermal SiO₂ surface is also studied by plan-view, high-resolution scanning electron microscopy at substrate temperatures ranging from 300 to 500°C. We have found that the saturation Ge island density is a strong function of substrate temperature, but a weak function of absolute Ge flux. This result suggests that Ge monomers can exist as a stable nucleus on thermal SiO₂.

8:20am **AS-FrM2 Chemical Vapor Deposition of WN_xC_y from Cl₃[Me₂NC(N^{super}iPr)₂]W(N^{super}iPr): Film Characterization and Evaluation for Diffusion Barrier Application**, H.A. Ajmera, A.T. Heitsch, L.L. Reitfort, C.B. Wilder, L. McElwee-White, T.J. Anderson, University of Florida

The tungsten isopropyl guanidinato complex Cl₃[Me₂NC(N^{super}iPr)₂]W(N^{super}iPr) (designated as 1) was used to deposit tungsten nitride carbide (WN_xC_y) thin films in a CVD reactor with deposition temperature ranging from 400 to 750 °C. The effect of deposition temperature on film properties such as composition, crystallinity, lattice parameter, grain size, growth rate and resistivity was studied. Films grown with 1 were composed of W, N, C and O as determined by Auger electron spectroscopy (AES). Film growth rate varied between 3 Å/min and 35 Å/min. The apparent activation energy in kinetically controlled growth regime was 0.49 eV. The films deposited below 500 °C were amorphous while films deposited at and above 500 °C were polycrystalline, with the peak position indicating presence of β -WN phase. Bonding information obtained from X-ray photoelectron spectroscopy (XPS) confirmed the presence of WN_xC_y phase in the film. Films deposited with 1 had a relatively small grain size (< 50 Å). To evaluate the efficacy of the deposited films as diffusion barriers, WN_xC_y thin film were coated with PVD Cu and vacuum annealed at 500 °C for 30 min. AES depth profiling and X-ray diffraction techniques were used to check for Cu diffusion through the barrier. WN_xC_y films deposited at 450 and 500 °C prevented Cu diffusion after vacuum annealing at 500 °C for 30 min. The film properties of thin films deposited with 1 and isopropyl imido complex Cl₃[R₂CN]W(N^{super}iPr) (2a, R = CH₃, 2b, R = Ph)¹ were also compared to provide insight on the effect of imido and guanidinato ligands on film properties. ¹FootnoteText@ ¹ Bchir O.J., Johnston S.W., Cuadra A.C., Anderson T.J., Ortiz C.G., Brooks B.C., Powell D.H., McElwee-White L., J. Crystal Growth 249 (2003) 262-274.

8:40am **AS-FrM3 RBS, ERDA and XPS Study of Ca_{0.28}Ba_{0.72}Nb₂O₆ Epitaxial Thin Films Prepared by PLD for Electro-Optical Applications**, P.F. Ndione, M. Kaidi, C. Durand, M. Chaker, R. Morandotti, Université du Québec, Canada

The development of integrated optic devices requires electro-optical materials with high transparency and good stoichiometry. Ferroelectric materials like strontium barium niobate (Sr_xBa_{1-x}Nb₂O₆, also called SBN-x) have been widely investigated because of their excellent electro-optical properties. Calcium barium niobate (Ca_xBa_{1-x}Nb₂O₆, also called CBN-x) possesses physical properties very close to those of SBN, while exhibiting a much higher Curie temperature (T_c higher than 250 °C for CBN single crystals). Therefore, CBN may be an excellent alternative to SBN for the realization of a new range of optical devices operating at high temperature. The fabrication of thin film is very attractive because it provides compatibility with integrated optical systems and other miniaturized devices and reduces their cost. Pulsed Laser Deposition (PLD) technique is suitable to grow complex oxides thin films, since it enable the preparation of stoichiometric and high quality epitaxial thin films. Nevertheless, oxygen deficiency or elements desorption from the surface of the films during the deposition process, lead to mixed valencies and other stoichiometric defects that modify the properties of the thin films. Therefore, it is very important to control the stoichiometry of thin films. Various surface analyses have been used for investigating the characteristics of ferroelectric thin films. In this paper, we present the composition, structure and chemical bonding states in CBN-28 thin films deposited at different oxygen pressure by PLD. A description of the elastic scattering processes which give rise to Rutherford backscattering spectroscopy (RBS) and Elastic Recoil Detection Analysis (ERDA) is given with particular attention paid to the complementarity of these two techniques for the detection of relatively heavy and light elements respectively. These analyses are completed with X-ray photoelectron spectroscopy (XPS) which give the chemical bonding states in CBN-28.

9:00am **AS-FrM4 Ion-Induced Effects during Reactive Sputter Deposition of ITO Films at the RF-biased Electrode**, A. Amassian, Cornell University; M. Dudek, O. Zabeida, J.E. Klemberg-Sapieha, L. Martinu, Ecole Polytechnique de Montreal, Canada

Research on tin doped indium oxide (ITO) has for many years been stimulated by the need to simultaneously optimize the electrical, optical and mechanical properties, and by new challenges related to the deposition on flexible plastic substrates. In the present work, we systematically studied ITO films deposited by reactive sputtering from an indium-tin alloy target. We found that additional radiofrequency (RF)-biasing at the substrate holder allows one to effectively control the level of stress in the film, as well as its crystalline structure, composition, electrical, and optical properties. A comparison of in situ real-time spectroscopic ellipsometry (RTSE) studies and elastic recoil detection (ERD) depth profiles revealed that even for samples with nominally identical compositional profiles, biased and unbiased films exhibit very different optical and electrical responses. Biased films exhibited a dense morphology with homogeneous n, k, and free carrier concentration depth profiles, whereas unbiased films exhibited columnar morphology, and large gradients of these properties. Using a novel Monte-Carlo TRIDYN simulation approach, which can model the ion bombardment effects of multi-component broad energy ion sources (e.g. RF plasma source and corresponding ion energy distribution function), we show that oxygen subplantation (shallow implantation) plays a crucial role in enhancing oxygen incorporation below the growth surface in the presence of biasing. This leads to both enhanced transparency in the visible spectrum, and an increase by an order of magnitude, of the free carrier concentration. We propose that atomic displacements resulting from intense ion-surface interactions in the presence of biasing are likely responsible for the activation of charge donors by a mechanism of oxygen vacancy formation.

9:20am **AS-FrM5 Electro Spray Deposition of Macro-Molecular Thin Films in High Vacuum Directly From Solution for Surface Science Applications**, M.M. Beerbom, Y. Yi, J.E. Lyon, A.J. Cascio, J.P. Magulick, R. Schlaf, University of South Florida

Electrospray is a widely used technique in mass spectrometry of large molecules since it leaves the injected molecules intact. We have adopted this technique for the deposition of macro-molecular thin films in high vacuum for surface scientific applications. Our results demonstrate the essentially contamination free deposition of a wide variety of macro molecular materials, such as conductive polymers, bio-molecules and nanoparticles. This allows the fabrication of clean thin films without the

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presence of ambient contaminants, enabling the use of vacuum based surface science techniques for their investigation. Previously, only ex-situ prepared macro-molecular thin films (or model systems, such as oligomers in lieu of polymers) could be investigated with these techniques. The main reason impeding evaporative deposition of macro-molecular materials under vacuum conditions is the thermal fragility and high molecular mass of these materials. In our presentation we will report about the performance of photoemission spectroscopic investigations in concert with multi-step in-situ electrospray deposition sequences for the investigation of macro-molecular interfaces. Our results demonstrate a deposition control similar to what can be achieved using in-situ evaporation.

9:40am **AS-FrM6 Characterization of Island Growth during Initial Stages of Atomic Layer Deposition of WNx on SiO₂**, *B.A. Carlson, N. Ramaswamy, P. Mrozek, S. Hues*, Micron Technology

Atomic layer deposited (ALD) Tungsten nitride (WNx) has been widely investigated for its application as gate electrodes, capacitor electrodes and barrier layers. For these applications, it is critical to understand the nucleation and growth behavior of WNx. In this paper we have investigated the initial stages of ALD WNx: nucleation, island growth and subsequent coalescence of islands to form a continuous film by various material characterization techniques such as time of flight secondary ion mass spectroscopy (TOF-SIMS), angle resolved X-Ray photo electron spectroscopy (ARXPS), atomic force microscopy (AFM), X ray reflectivity (XRR) and electron probe microanalysis (EPMA). A simple phenomenological model based on surface area of islands during nucleation, growth and coalescence has been formulated to describe island growth in ALD. Symposium on VLSI Technology, 2004, Park, M. Lee, K. Moon, H. Lee, and H. Kang, IEEE International, Interconnect Technology Conference, Proceedings, San Francisco, 1-3 June, 1998, pp. 96-98. Takeyama and A. Noya, Jpn. J. Appl. Phys., Part 1 36, 2261, 1997.

10:00am **AS-FrM7 Structural Characterization of HfO₂ Based Silicon CMOS Stacks**, *M. Copel*, IBM Research Division **INVITED**

The use of new materials for gate dielectric and metal gates, the very core of an FET, poses serious materials challenges. Most of the problems are first encountered by electrical characterization, however it is often a matter of structural characterization to understand and solve the problems. Typical difficulties involve capacitance loss, poor mobility, and incorrect device operating thresholds. This talk will highlight how analytical capabilities can guide our thinking on these problems using techniques such as medium energy ion scattering (MEIS), x-ray photoemission spectroscopy (XPS) and other methods. Generally, capacitance loss can be traced to growth of interfacial oxide, which can be detected by numerous methods. Finding the source of excess oxygen may involve detailed process learning and strict control of oxygen contamination throughout the gate stack. Mobility degradation is a more elusive problem, since many factors can come into play. I will show one example where depth profiling in HfSiO_x using MEIS provides crucial information: non-uniform Si content correlates with poor performance. Perhaps the most difficult analytical challenge is posed by threshold voltage characteristics, which are dominated by dielectric charge and work function alterations. So far, we can only indirectly measure the problem through band offset measurements without directly sensing the defects responsible for the problem. There is a tremendous opportunity for materials characterization to resolve the problems faced by the microelectronics industry. This talk will outline some of the ways we can meet this challenge.

10:40am **AS-FrM9 Back Side SIMS Depth Profile Analysis of a High-k Dielectric Material**, *F.A. Stevie, R. Garcia, Z. Zhu*, North Carolina State University; *P. Sivasubramani, R.M. Wallace*, University of Texas at Dallas; *D.P. Griffis*, North Carolina State University

Current status of the back side SIMS depth profiling method and results on a high-k dielectric material are presented. A typical concern for high-k materials is diffusion of the constituent elements into underlying silicon during CMOS activation annealing. High-k dielectric materials are difficult to depth profile from the front side because of non-uniform sputtering and the necessity to analyze an element at a trace level after profiling through a layer with a matrix level concentration of the same element. Mechanical polishing was used to reach the area of interest. A successful back side polishing experiment requires that the polished surface be flat, smooth and parallel to the front side surface with as thin a residual cover layer as possible. Analytical concerns include sample mounting, optimization of depth resolution, and control of sample charging. The material under study is HfAlON. SIMS

depth profile analyses were performed using a magnetic sector CAMECA IMS-6F. Application of a ruthenium conductive layer to cap the sample not only reduced sample charging, but proved to be a good choice for adherence of the conductive layer to the sample surface and to the non-conductive mounting epoxy. Samples of the dielectric before and after 10 sec RTA anneal at 1000 °C were prepared for SIMS analysis using mechanical polishing. Neither sample showed measurable Hf or Al diffusion into the silicon substrate. Sivasubramani, M. J. Kim, B. E. Gnade, R. M. Wallace, L. F. Edge, D. G. Schlom, H. S. Craft and J.-P. Maria, Applied Physics Letters 86, 201901 (2005). C. Gu, A. Pivovarov, R. Garcia, F. Stevie, D. Griffis, J. Moran, L. Kulig, and J. F. Richards, J. Vac. Sci. Technol. B22, 350 (2004).

11:00am **AS-FrM10 Copper Diffusion Barrier Performance of PEALD TaSiNC**, *W. Zeng, E.T. Eisenbraun*, University at Albany - The State University of New York

Continued downscaling of device dimensions has placed a high priority on the development of robust copper barrier/liner materials. Diffusion barrier requirements for shrinking device dimensions are very rigid, which include prevention of copper diffusion, good thermal/chemical stability, low resistivity, amorphous structure, etc. Moreover, the associated process used to deposit these materials needs to be carried out at reduced temperatures to allow integration with low-k materials which are mostly thermally fragile polymers, and are required to yield smooth, conformal films in aggressive trench/via structures, with atomic layer scale thickness and uniformity control. In this respect, atomic layer deposition (ALD) is emerging as a highly promising copper barrier/liner deposition technique, due to its inherent excellent step coverage and precise thickness control. In this work, a novel low temperature PEALD process for the growth of TaSiNC films has been developed employing a Genus Stratagem 200-mm wafer capable PEALD tool using TBDET and trichloromethylsilane. The films were characterized using RBS, AES, XRD, SEM, AFM, ellipsometry, and four-point resistance probe. It was found that Si incorporation influenced both the resistivity and crystal structure of the PEALD TaSiNC films. As silicon content was increased from 0 to 11 at. %, resistivity increased from 270 μΩ/cm to 3380 μΩ/cm, while the texture changes from a nanocrystalline structure with an average grain size of 14 nm to an amorphous structure. The first pass copper diffusion barrier performance study of 5 nm-thick TaSiNC films, possessing a range of Si contents, determined that all films could prevent copper from diffusing into Si substrates after annealing Cu/TaSiNC/Si stacks at 500°C in 700 torr Ar ambient for 30 minutes irrespective of Si content. These results and proposed barrier failure mechanisms are discussed.

11:20am **AS-FrM11 Synthesis and Characterization of Nanoscale Al-Si-O Gradient Membranes for Gas Analytical Microdevices**, *M. Bruns, V. Trouillet, E. Nold*, Forschungszentrum Karlsruhe GmbH, Germany; *R.G. White*, Thermo Electron Corporation, England

A microarray of 38 identical sensor elements on an area of 4x8mm² is the key element of the Karlsruhe micro nose. It is based on a Pt-doped SnO₂ layer, the electrical conductivity of which is highly sensitive to the composition of the ambient atmosphere and is measured between adjacent parallel platinum strip electrodes. In order to enable pattern recognition techniques these sensor elements have to be gradually differentiated with respect to their gas response. For this purpose gas-permeable membranes with thickness variation of approximately 2 to 10 nm were deposited across microarray using ion beam induced chemical vapour deposition. This paper focuses on mixed Si-Al-O membranes combining the gas permeability of silica with chromatographic properties of alumina. Shaping of the ion beam profile gradually alters the ion current density and leads to laterally different deposition rates forming the membrane gradient as a projection of the ion beam profile. Various Al/Si concentration ratios within the membrane and even concentration gradients across the array can be obtained by tuning the array temperature during deposition. We present a comprehensive characterization of differently shaped nanoscale membranes with different Al/Si concentration ratios and gradients. Auger electron spectroscopy is used for the evaluation of the geometrical integrity of the uncoated electrode pattern and for the determination of thickness profiles, respectively. Parallel angle resolved X-ray photoelectron spectroscopy provides thickness information for the membranes together with information on chemical binding states in a non-destructive manner. Ellipsometry is a powerful quantification method for the determination of the desired ultra thin membrane thickness profiles. Moreover, after calibration with surface analytical data, ellipsometry allows for rapid evaluation of Al/Si concentrations ratios within the membranes.

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11:40am **AS-FrM12 Studies of Vanadium Pentoxide Thin Films as a Function of Number of Lithium Ion Intercalation Cycles**, *J.E. Castle*, University of Surrey, UK; *A.M. Salvi*, *N Ibris*, Universita' della Studi della Basilicata, Italy; *D. Alamarguy*, Laboratoire de Genie Electrique de Paris, France

The intercalation of vanadium pentoxide by lithium ions leads to a change in optical properties, a process that is of value in thin-film electrochromic devices. The extent of intercalation can be measured, electrochemically, from the charge capacity of the film, and is in good agreement with that determined spectroscopically by X-ray photoelectron spectroscopy (XPS). On de-intercalation there is again good agreement. However XPS might not be able to detect low level of Li retained in trapping sites within the film. Since such retention could be a source of chemical degradation we have examined the concentration of lithium ions, either within the lattice or at boundaries and interfaces within the structure, by depth profiling using secondary ion mass spectrometry (SIMS). SIMS is a valuable tool for the analytical determination of Li, for which it has excellent sensitivity. In this study films of V₂O₅ deposited on ITO-glass coupons by a sol/gel process were challenged by increasing numbers of charge-discharge cycles, ranging from 72 to 598 full cycles. The samples were characterised by XPS and then examined in the de-intercalated state by ToFSIMS. The lithium depth profiles for four samples are compared. These profiles are broadly similar, with a marked build up of Li at the interface with the indium tin oxide (ITO). Although lithium is retained, the integrated quantity is very small and below detection by XPS. However the profiles are of interest because of the marked accumulation of Li at the interface with ITO.

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