

Tuesday Afternoon Poster Sessions

Applied Surface Science

Room: Central Hall - Session AS-TuP

Applied Surface Science Poster Session

AS-TuP1 Sub-Micrometer Imaging of Lipids and Trace Elements in Various Cells with ToF-SIMS and Laser-SNMS. *H.F. Arlinghaus, F. Draude, S. Galla, A. Pelster, M. Körsgen*, University of Muenster, Germany, *J. Tentschert, H. Jungnickel, A. Haase, A. Luch*, German Federal Institute of Risk Assessment, Germany, *T. Schwerdtle, J. Muthing*, University of Muenster, Germany

In recent years, molecular imaging with submicron lateral resolution has become of more and more interest for characterizing specialized compounds in biological samples. As an example, nanoparticles (NPs) gain great commercial interest in the medical field due to their high mobility in human tissue. Despite broad applications close to the human body, so far, there is only little knowledge of possible toxicity. In this context, the distribution of NPs within cells is of particular interest. Moreover, not only the distribution of NPs but also elemental and molecular cellular distributions such as metabolites and lipids are interesting for medical research.

In this study, we used time-of-flight secondary ion mass spectrometry (ToF-SIMS) and laser-secondary neutral mass spectrometry (Laser-SNMS) to investigate different cells both unexposed and exposed in vitro to silver NPs (AgNPs) and arsenic species. To optimize the analysis, a special silicon wafer sandwich preparation technique was employed; this entails freeze-fracturing and washing of cell cultures that were grown on silicon wafers. The data showed that during freeze-fracturing, the cell membrane is often stripped from the cell, enabling direct analysis of the interior of the cells on one sandwich wafer and the remaining lipid membrane as a mirror image on the opposite wafer. During analysis, the signal from the nutrient materials was observed to diminish the contrast of the molecular signals in the images. By optimizing the preparation and washing procedures, both the contrast and the imaging resolution could be significantly increased due to higher molecular yields and lower background. With these optimization procedures it was possible to detect lipid ions in a higher mass range, especially from those membranes that were stripped from the cells.

Under these optimized conditions, several studies were performed to detect the distributions of trace elements in cells. One study dealt with AgNPs. In this context the uptake of AgNPs of human macrophages was measured with nanometer-scale resolution. 2D and 3D Laser-SNMS images clearly showed that AgNPs are incorporated by macrophages and in part agglomerate to silver aggregates with a diameter of ~3-7 μm . In a similar approach, the distribution of arsenic in cells was measured to obtain more information on the reasons why inorganic arsenic proves carcinogenic in humans. A comparison with ToF-SIMS data showed that especially the high elemental sensitivity of Laser-SNMS makes it possible to detect these trace elements in cells.

AS-TuP2 Comparative Study on the Methods to Determine the Interface Locations in SIMS Depth Profiling Analysis of Multilayer Films. *H.H. Hwang*, University of Science and Technology (UST), Republic of Korea, *J.S. Jang, H.J. Kang*, Chungbuk National University (CBNU), Republic of Korea, *K.J. Kim*, University of Science and Technology (UST), Republic of Korea

In-depth analysis by secondary ion mass spectrometry (SIMS) is very important for the development of electronic devices using multilayered structures, because the quantity and depth distribution of some elements are critical for the electronic properties. Correct determination of the interface locations is critical for the calibration of the depth scale in SIMS depth profiling analysis of multilayer films. However, the interface locations are distorted from real ones by the several effects due to sputtering with energetic ions.

In this study, we compared the three definitions for the determination of interface locations in SIMS depth profiling of multilayer films. Especially, we investigated the feasibility of 50 atomic % definition for Si/Ge and Si/Ti multilayer films by various SIMS analysis parameters. In 50 atomic % definition, the original SIMS depth profiles are converted into compositional depth profiles by the relative sensitivity factors (RSF) derived from the alloy reference films with well-known compositions determined by Rutherford backscattering spectroscopy (RBS).

The application of the 50% definition determined from the ion intensities was found to be very limited to specific systems showing clear interfaces. The definition of the interface by the dimer ions between the atoms in the two different layers was also difficult to apply due to the small intensity and the unclear variation at the interfaces.

AS-TuP3 Estimation of Useful Yield of Electrospray Droplet Impact/Secondary Ion Mass Spectrometry. *R. Takaiishi, K. Hiraoka*, University of Yamanashi, Japan

The electrospray droplet impact secondary ion mass spectrometry (EDI/SIMS) has been developed as cluster SIMS[1]. EDI utilizes charged water droplets generated by ambient electrospray. The typical droplet is represented as $[(\text{H}_2\text{O})_{90,000} + 100\text{H}]^+$ with mass of $\sim 10^6$ u. The kinetic energy of droplets is about 10^6 eV with the velocity of 12 km/s. EDI/SIMS has the atomic/molecular level etching abilities[1][2]. EDI/SIMS was found to be applicable to many kinds of inorganic and organic material [1][3]. In spite of the shallow surface etching, relatively high secondary ion yields can be obtained by EDI.

The high ionization efficiency may be due to the occurrence of supersonic collision taking place between the droplet and the sample surface. In order to estimate the useful yield (i.e., total ions generated divided by the total molecules desorbed), mass spectra were measured for binary mixtures of C_{60} /Rhodamine B (1:1) and C_{60} /Aerosol OT (1:1). The equimolar samples were crushed and mixed in mortar and deposited on a stainless steel target as thin films using a spatula. This method was adopted from solvent-free MALDI. By assuming that (1) the desorption efficiency is the same for C_{60} , Rhodamine B and Aerosol OT, and (2) the desorbed ionic compounds directly give secondary ion signals, the useful yield was crudely estimated to be ~ 0.1 . This high value explains the high ionization efficiency of EDI/SIMS.

Reference

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AS-TuP4 Multivariate Analysis Models to Predict Surface Chemistry or Performance using ToF-SIMS Mass Spectra Datasets. *N. Sano, M.-L. Abel, J.F. Watts*, University of Surrey, UK

Latent (that is unintentional) adhesion between organics and inorganic surfaces is a well known phenomenon in many areas of materials science, e.g. the moulding of polymeric components and the storage of coated metal products where a polymeric surface is in intimate contact with the back of another sheet. A complete understanding of the adhesion and adhesion processes that occur at this interface may provide a key to obtaining optimum performance for a particular application.

In this work, we are considered with the effects of migration of organics to the surface of the polymeric host and their role at the polymer/inorganic interface. We have focused on three characteristic organics widely used as additives in a wide range of polymer formulations. In the samples we have studied, characteristic peaks from these additives dominate the ToF-SIMS analysis of the inorganic surface. In addition, surface chemistry of the inorganic surface induces different mechanical performances of the products. The storage period has the potential to play a significant role in the migration of minor components towards the interface under investigation, and data will be presented at two different periods (early and late stages).

In this study we show models using multivariate analysis describing how ToF-SIMS analysis can be applied to understand the surface chemistry of industrial materials. The behaviour of migration from the polymer to the inorganic side of the polymeric assembly induces three characteristic surface chemistries which influence mechanical performance. Our models show good predictions for a validation sample of materials.

AS-TuP5 Method for Cross-sectional Analysis Using FIB, ToF-SIMS and Multivariate Analysis. *J.A. Ohlhausen, M.J. Rye, P.G. Kotula, J.R. Michael, T.J. Garino*, Sandia National Laboratories

We have developed a method to create a cross-section of small samples for Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) utilizing a Focused Ion Beam (FIB) approach. Using this method, a nearly ideal surface for elemental and molecular analysis of the cross-sectional surface is produced, thus providing complimentary information to other microanalytical techniques like scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM).

FIB is commonly used to create cross sections for SEM and STEM imaging and analysis. Benefits of this technique include controlled extraction area and high spatial resolution. Unfortunately, elemental analyses in the SEM and STEM are not sensitive to low-Z elements and have detection limits that may prevent the detection of some species of interest. Although ToF-SIMS produces lower spatial resolution ($\sim 200\text{nm}$), it has excellent low-Z

sensitivity and has detection limits in the ppm to ppb range. Traditional FIB lift-out sections have been used as cross sections for ToF-SIMS analysis, but they are typically fragile and difficult to handle, thus complicating ToF-SIMS analysis. We have developed a method to create cross sections of particles and small fragments of material that can be analyzed in the “as cut / as mounted” condition. Samples are placed on a traditional SEM mount, and then coated with a conductive layer of AuPd. With the use of special mounts, a cross section that is parallel to the sample surface is milled in the FIB. The resulting samples are sturdy, allowing the removal of the Ga implants by O₂ sputtering. The cross sectioned sample can now be analyzed with ToF-SIMS. Using data from ZnO multi-grain particles, we will show that ToF-SIMS analysis of the cross section yields elemental and molecular information with low detection limits. Additionally, we will demonstrate that multivariate analysis of ToF-SIMS data acquired by this technique is complimentary to a FIB-STEM analysis.

§Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

AS-TuP6 XPS Depth Analysis of Metal/Polymer Multilayer by Electro Spray Droplet Impact, Y. Sakai, R. Takaishi, S. Ninomiya, K. Hiraoka, University of Yamanashi, Japan

The electro spray droplet impact (EDI) has been developed for cluster SIMS [1]. EDI utilizes the charged water droplets as projectiles for reducing the sample surface degradations often encountered in atomic-ion SIMS. EDI projectiles are extremely large water cluster ions generated by an ambient electro spray (masses of several 10⁶ u). EDI is capable of atomic- and molecular-level etching with little damage after the irradiation. The EDI gun has been installed in X-ray Photoelectron Spectroscopy (XPS) instrument to analyze the dynamic etching processes during the EDI irradiation. This system has been applied to various organic and inorganic materials. A comparative study of Ar⁺ and EDI etching was performed. While selective etching was observed for almost all of the samples examined by Ar⁺, no chemical modification was recognized by EDI [2,3]. The multilayer metal/polymer samples are used for many practical applications such as transducer, optical device and packaging, etc. For example, the metal layers in integrated circuits are used as the electrical connection and barrier. The interface analysis of metal/ polymer multilayer is of significant importance to clarify the diffusion phenomena taking place between metal and polymer interface. Thus, the ion gun for the interface analysis that is capable of molecular-level etching with no chemical modification is highly demanded. Our preliminary experimental data showed that the EDI gun is very useful for metal/polymer interface analysis. In this report, the depth analysis of Cu/Polymer/Si by EDI etching will be presented. Reference [1] K. Hiraoka, D. Asakawa, S. Fujimaki, A. Takamizawa, K. Mori, Eur. Phys. J. D 38, 225 (2006) [2] Y. Sakai, Y. Iijima, D. Asakawa and K. Hiraoka, Surf. Interface Anal. 42, 658 (2010) [3] Y. Sakai, S. Ninomiya and K. Hiraoka, Surf. Interface Anal. 43, 1605 (2011)

AS-TuP7 A Combined HAXPES and Electrical Characterisation Study of Si and III-V based MOS Structures, L.A. Walsh, G.J. Hughes, Dublin City University, Ireland, P.K. Hurley, J.H. Lin, Tyndall National Laboratory, Ireland, J.C. Woicik, National Institute of Standards and Technology

The aim of this study was to use synchrotron radiation based HAXPES measurements to study the intrinsic electronic properties of both Si and III-V based MOS structures. High quality thermally grown SiO₂ layers, with a thickness of 8 nm, were grown on both n (5x10¹⁵ cm⁻³) and p (5x10¹⁵ cm⁻³) doped silicon. While Al₂O₃ layers 8nm thick were deposited on both n (Si - 5x10¹⁷ cm⁻³) and p (Zn - 5x10¹⁷ cm⁻³) doped GaAs, and n and p (~4x10¹⁷ cm⁻³ for both) doped InGaAs substrates. All substrates were treated by a wet chemical ammonium sulphide based passivation treatment. The samples for HAXPES analysis were capped with 5 nm Ni or Al blanket films by electron beam evaporation. For electrical characterisation, Ni/Au (70 nm/90 nm) and Al (160 nm) gate electrodes were patterned by electron beam evaporation and a lift off lithography process. HAXPES measurements using a photon energy of 4150 eV were used to probe the MOS structures in order to investigate the differences in substrate core level binding energies caused by changes in doping type, and metal work function. The sampling depth for these high energy photons was sufficient to detect core level peaks originating from the substrate, the 8 nm thick dielectric layer, and the top metal contact. The binding energy of core levels in photo emission are referenced with respect to the Fermi level, therefore changes in the binding energy of a particular core level reflect differences in the position of the Fermi level in the semiconductor band gap. For the MOS structures fabricated using SiO₂/Si, changes in the Fermi level positions and differences in the potential drops across the dielectric layers have been directly correlated with the metal workfunction differences observed in the

CV and GV measurements. A binding energy difference of 0.6 eV was measured between the GaAs core levels of the n and p doped substrates, independent of metal work function indicating the strong Fermi level pinning present at the Al₂O₃/GaAs interface. Binding energy measurements for the core levels of native oxide covered n-type doped InGaAs substrates with no metal cap were found to be consistently (~0.3 eV) higher than p-type samples reflecting the fact that the Fermi level is in a different position in the band gap. A binding energy difference of 0.25eV for the core levels of the n and p samples just with the Al₂O₃ dielectric layer present, indicating different Fermi level positions in the band gap. Deposition of the different workfunction metals resulted in limited change in the InGaAs core level binding energies, indicating the partially pinned nature of the Al₂O₃/InGaAs interface.

AS-TuP9 The Development of Charged Particle Lenses for High Spatial Resolution XPS Studies, R. Walker, Shimadzu Research Laboratory (Europe) LTD, UK

The development of selected area and imaging XPS made significant advances with the adoption of Magnetic Snorkel lenses. This lens type of an unconventional design, projects from its main bulk an axial magnetic field that enables focusing of charged particles with low optical aberrations. Simulation techniques, calculate typical lens aberration coefficients of spherical, Cs=3mm and chromatic, Cc=8mm. In the XPS application original theoretical expressions used to characterize this lens type, have been re-modeled, to use present day data and predict some future improvements with this and other lens types. The spatial resolution of present commercial instruments (3µm) is limited by signal to noise. With the large collection angles involved, it is shown that astigmatism is a major contribution that limits the spatial resolution. Furthermore the spatial resolution of the detected signals is insufficient to resolve the stigmatic foci of the astigmatism present in the XPS image. Snorkel lenses are positioned under the specimen and to enable sufficient working distance between the lens and the specimen surface, the lens is highly excited. Typical working distances measure 15mm. By refining the lens coil and iron circuit design, the lens excitation is increased to a maximum and a lens working distance of 19mm is achieved. Consequently with the Snorkel lens positioned in this manner, the thickness of sample will remain limited. A Snorkel lens may also be positioned above the specimen surface so that previous spatial constraints imposed on the specimen form no longer apply. The lens is conical in shape with a bore to focus the photoelectrons through. It will be shown that a Snorkel lens with a 45° access to the specimen surface and at a 2mm working distance has been experimentally proved with very low lens aberration coefficients (Cs, Cc) of 1mm. Calculations show that with only small increases to existing laboratory x-ray powers, it is possible to use this lens to image XPS spatial resolutions of 1µm with present day count rates. Snorkel lenses can have limitations with specimens that magnetize, particularly specimens with topography. Substitution of an Electrostatic accelerating lens for a Magnetic Snorkel lens may result in only a small deterioration of the detected photo electron photoelectron spatial resolution. The ultimate spatial resolution of an image exhibiting the same signal to noise is calculated to be 7µm (Electrostatic) as opposed to 3µm (present day Magnetic). Details of an accelerating electrostatic lens are shown, that is proved to operate reliably with no electrical breakdown.

AS-TuP10 Image Depth Profiling for Three-Dimensional Characterisation of Microelectronic Structures, B. Sgammato, A.E. Wright, A. Bushell, Thermo Fisher Scientific, UK

Microelectronic devices typically consist of elaborate three-dimensional structures, and careful control of chemical and structural properties is required for effective operation. Structures such as pads and bond pads must be carefully assessed for correct size, composition, layering and contamination levels. Supporting structures and substrates must also have the correct composition, integrity and electronic properties.

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive material characterisation technique that offers sensitive chemical state information, and is already established as a method of choice for the analysis of microelectronic devices. Parallel XPS imaging offers high spatial resolution for observing the lateral distribution of chemical states at the surface of a material, and recent advances in spectroscopic imaging allow the generation of quantitative chemical state images for maximal information content.

Depth profiling, typically with ion beams, allows the gradual removal of material from a sample surface, so that XPS can be used to probe further than its characteristic nanometre-scale analysis depth.

The combination of spectroscopic parallel imaging and depth profiling, using the Thermo Scientific Escalab250Xi, permits unmatched spatial resolution combined with layering information, and permits the clear identification of subsurface structures and chemical states. The powerful, intuitive Avantage software datasystem makes data processing

straightforward, so that profile information from small parts of the sample are simple to generate.

AS-TuP11 Developing a Methodology for XPS Profiling of Biofilms and Biological Materials, *R.G. White*, Thermo Fisher Scientific, UK, *D.Y. Petrovykh*, International Iberian Nanotechnology Laboratory, Portugal, *A.C. Areias*, *C. Sousa*, *G.P. Mendes*, University of Minho, Portugal

Films of cells on solid substrates are encountered in a variety of biological and biomedical environments, including cells in biofilms that spontaneously colonize medical devices and multilayers of cells filtered from suspensions for analysis. Understanding the chemical properties of cells in such films is important for providing clues about the behavior of the cells or about the effects of treatments that had been applied to the cells.

X-ray Photoelectron Spectroscopy (XPS), with its combination of chemical selectivity and surface specificity, is an ideal technique for analysing these biofilms and multilayers, but it needs to be combined with profiling to more fully characterise the samples. It is well known that profiling with traditionally used argon monomers results in a high degree of chemical modification for most organic materials. Recent studies have shown, however, that argon cluster beams may be used for depth profiling of organic materials while preserving the chemical information.

This poster will present data from cluster profiling studies of biofilms and biomaterials. The methodology required for optimum profiling of these samples will be discussed, including an evaluation of XPS data acquisition protocols, as well as sputtering conditions.

AS-TuP12 XPS and Auger Analysis of Single and Multi-Layer Graphene Films: What is Graphene and What is Not?, *H.M. Meyer III*, *I. Vlasiouk*, Oak Ridge National Laboratory, *A.V. Sumant*, Argonne National Laboratory

Graphene has received unprecedented attention since 2010 when the Nobel Prize was awarded to Geim and Novoselov for “groundbreaking experiments regarding the two-dimensional material graphene.” Many graphene-related publications use the C 1s spectrum to demonstrate the existence or formation of graphene, but unique photoemission spectral signatures are difficult due to the inherent thinness of single or even multi-layer graphene. The difficulty is due to the surface sensitivity of XPS and Auger spectra and the analysis of spectra that include graphene, substrate-related carbon and possible adsorbed carbonaceous material on the graphene. This poster explores various XPS and Auger spectral features from studies of graphene grown by the CVD method on Cu (near-single layer) and Ni (multi-layer). In one study, graphene grown on Cu was heated in air to determine if the graphene provided any protection to the underlying Cu substrate. The results indicated not only oxidation (i.e. corrosion) protection, but that there was a time and heat dependence of the protection. To aid in the understanding of graphene vs. substrate contributions to the C 1s XPS spectrum, additional studies were performed on CVD-grown diamond substrates. Diamond substrates (very low oxygen and pure sp³-type carbon) offer an interesting contrast to most substrates that have inherent O and C contributions to the O 1s and C 1s spectra. Unique XPS and Auger related features of graphene will be highlighted in this poster.

AS-TuP13 XPS Sputter Depth Profiling of Organic Thin Films Using an Ar Cluster Ion Source, *A.J. Roberts*, *S.J. Hutton*, *C.J. Blomfield*, *W. Boxford*, Kratos Analytical Ltd., UK

A new 20 keV Ar cluster ion source has been used to successfully sputter profile through a range of organic thin films and multilayers. Samples were analysed using XPS between sputter cycles to allow the chemical composition of the sample to be probed as a function of depth into the material. Use of massive Ar cluster ions (1000 to 2000 Ar atoms per ion) promote the retention of sample chemistry throughout the depth profile. In this study we report the performance of the Ar cluster ion source on a range of organic thin films, from fields as diverse as organic PV materials, OLED's, cross-linked plasma polymers and multilayers. Analysis conditions were optimised to maximise retention of chemical functionalities and minimise ion induced interlayer broadening.

AS-TuP14 Quantitative XPS Depth Profiling of Mobile Ions in Soda-Lime-Silica Glasses using a Polyatomic Ion Source, *C.J. Blomfield*, *S.J. Hutton*, *W. Boxford*, Kratos Analytical Ltd., UK

Soda-lime-silica glass is widely used not only for architectural and automotive applications but increasingly in electrical devices as display panels and in photovoltaic applications. The role of mobile ions such as alkali or alkaline-earth ions in these glasses can affect the quality in architectural glass but can have a large impact on electrical device performance. It is important to know the concentration of these mobile ions in the glass surface region and deeper into the glass substrate to understand the leaching process.

Alkali migration has been a noted artefact of sputtering with monatomic Ar ion beams and the use of polyatomic ion beams more commonly applied to organic materials has been shown to yield some benefits in reduced migration without incorporation of C into the glass matrix.

In this investigation we compare the results with monatomic Ar ion sputtering and polyatomic (Coronene) for a number of soda-lime-silica glass samples.

AS-TuP15 XPS Assessment of the Thickness of Fe Oxide Layers using Standard and Active Shirley Background, *M. Bravo-Sanchez*, CINVESTAV-Unidad Queretaro, Mexico, *F. Espinosa-Magaña*, CIMAV Unidad-Chihuahua, Mexico, *A. Herrera-Gomez*, UAM-Azcapotzalco and CINVESTAV-Queretaro, Mexico

The thickness of metal oxide nanolayers can be assessed through X-Ray Photoelectron Spectroscopy (XPS) measurements. This is done by comparing the signal from oxide and metallic XPS peaks. The correct assessment of the oxide layer thickness depends on how accurate the peak areas are quantified through peak fitting. Since the oxide and metallic peaks overlaps in XPS spectra, the calculation of their areas could be tricky. This is specially the case for iron since the Fe 2p peak, which is the iron peak most employed in XPS experiments, is largely asymmetric. In this work, we show that the assessment of the peak areas can carry errors as large as 120% if the traditional Shirley background is employed. The problem is solved by the use of the “active” background removal method, in which the background intensity is optimized during the peak-fitting process. This method is described in detail, as well as its software implementation. The results are supported with High Resolution Transmission Electron Microscopy micrographs.

AS-TuP16 Active Fitting for Optimized Shirley Background Determination, *J. Muñoz-Flores*, UAM-Xochimilco, Mexico, *A. Herrera-Gomez*, UAM-Azcapotzalco and CINVESTAV-Queretaro, Mexico

To subtract the Shirley background to X-Ray Photoelectron Spectroscopy data it is necessary to choose two points, one at each side of the main features of the spectrum. It is common that these points are set close to the peaks to avoid other features present in the spectrum or simply because the data was not acquired with a wide enough energy range. The latter is a common error since it is difficult to discriminate by eye where the contribution of the peaks becomes negligible and the signal is completely due to the background. This is particularly true for peaks with large kurtosis (i.e., large Lorentzian widths) and even more for asymmetric peaks. In the traditional Shirley method, the background is forced to pass through the set points, not allowing any contribution of the peaks to the total signal at those points. As a consequence, the area of the peaks is usually underestimated. In this work we describe the error in the quantification of the peak areas as a function of the energy range and peak width when the traditional Shirley method is applied. This type of error can be avoided if the intensity of the Shirley background is optimized during the peak-fitting procedure, without the restriction of the background passing through the set points. This “active” method is described in detail, as well as its software implementation. By the use of simulated data, it is shown that the active method assesses the peak areas very precisely even when the data is obtained with a too-short energy range.

AS-TuP18 Atom Probe Tomography Analysis of Grain Boundaries in CdTe, *V.S. Smentkowski*, General Electric Global Research Center, *D.J. Larson*, *D.A. Reinhard*, *T.J. Prosa*, CAMECA Instruments Inc., *D. Olson*, Cambridge University, UK, *D. Lawrence*, *P.H. Clifton*, *R.M. Ulfir*, *T.F. Kelly*, CAMECA Instruments Inc.

Photovoltaic materials convert photons to electrical energy (e.g., solar cells) or convert electrical energy into light (e.g. light emitting diodes). Films based on the II-VI compound CdTe are currently regarded as one of the leading type II materials for development of cost-effective solar cells as the CdTe band gap is near ideal for photovoltaic conversion efficiency [1]. While theoretical efficiency values approach 30% [2], commercial and laboratory tests of CdS/CdTe heterojunctions range from ~10% to ~17%, respectively [3,4]. The presence of grain boundaries in these structures likely plays an important role in the observed efficiency. In the current work we investigate, for the first time, the applicability of atom probe tomography (APT) to characterize grain boundaries within the CdTe layer of a solar device. APT data were collected on a CAMECA LEAPTM 4000X HR operated at a base temperature of 40K with a laser energy of 3pJ, a repetition rate of 100kHz and an ion detection rate of 1%. Specimens for APT were prepared by standard focused-ion-beam milling methods [5] from a CdTe layer within a solar cell. Laser-pulsed APT spectra from CdTe-based alloys are quite complex [6,7]. There are two reasons for this: 1) Cd and Te each have eight isotopes and 2) Cd and Te field evaporate in a multitude of complex molecular ions species. The following ions were detected in mass spectra: Cd⁺, Te⁺, CdTe⁺, Cd₂⁺⁺, and Te₂⁺⁺, Cd₂Te⁺⁺ and

CdTe₂⁺⁺, Cd₂⁺, CdTe⁺ and Te₂⁺. In spite of the complex nature of these spectra, all of the peaks are identifiable as some combination of Cd and/or Te. This poster will show both the measured spectra and CdTe composition estimate, as well as 3D images revealing enhancement of S and Cl at a grain boundary.

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AS-TuP19 Mapping of a Natural Lubricant Network on the Surface of Silicone Hydrogel Materials Using Surface and Bulk Chemistry Techniques, K.A. Wygladacz, D.J. Hook, M. Merchea, E.P. Maziarz, Bausch + Lomb

Commercial silicone hydrogel contact lenses (SiHy) are ophthalmic devices designed to correct vision as well as function as an ocular bandage for therapeutic purposes. Surface wettability, modulus, surface topography as well as bulk water content are some of the factors that influence lens comfort and performance. Contact lens surface wettability is believed to be an important factor in comfort as well as overall patient satisfaction. Tear confluence across a lens surface may be improved by the presence of well-chosen biomolecules, capable of retaining moisture. Very recently the application of a natural lubricant hyaluronate (HA), to a daily use multi purpose solution (MPS), Biotrue™ has been reported.

In these studies HA was used in conjunction with a surfactant system present in Biotrue™ MPS. The exclusive formulation of Biotrue™ was designed to improve hydration and wettability of various SiHy contact lens materials. Improvements in moisture retention are attributed to the use of high molecular weight HA present in Biotrue™ capable of high water retention. Presence of HA on a lens surface acts as a wetting agent and improves the properties of SiHy contact lens materials. To our knowledge there is no published literature reporting on a visualization method of HA on SiHy contact lenses surfaces.

The purpose of this research was to develop a direct method to demonstrate the presence of a HA network on the surface of SiHy contact lenses using surface chemistry techniques. Senofilcon A® and balafilcon A® were chosen to investigate the interaction of HA with SiHy materials. Atomic Force Microscopy (AFM) was applied to examine the topography of both materials in the hydrated and dehydrated state. The visualization of HA chains was done using Confocal Laser Scanning Microscopy (CLSM) and Differential Interference Contrast (DIC) microscopy using a dye selective for HA (Safranin).

Senofilcon A® and balafilcon A® were soaked in Biotrue™ for 4 hours. Lenses were then soaked in 3 mL of Safranin solution. After 3 min the samples were rinsed with DI water for 3 min to remove any unbound dye. Samples were imaged using an Olympus CLSM equipped with a DIC attachment. Individual confocal images were captured using an air objective sequentially across the sample. A large mosaic was generated using fiducial marks stitched together from the individual images. SiHy lenses incubated with Safranin solution but not exposed to Biotrue™ were characterized as control. Additionally applicability of X-ray Photoelectron Spectroscopy (XPS) for HA mapping on the lenses surface was examined. AFM was used in parallel to study modification of the lens surfaces with HA biopolymer.

AS-TuP20 Kinetics and Mechanism Studies of Copper Nano-Structures Formation on Functionalized Si Surfaces, J.M. Lin, University of Delaware, K.A. Perrine, University of California, Irvine, A.V. Teplyakov, University of Delaware

The manufacture of modern electronic devices has been longing for the higher control over chemical deposition processes and interface properties, as the electronic devices kept scaling down. As a result, a comprehensive understanding of surface reaction mechanisms between the precursor molecule and surface reactive sites is desired.

Numerous studies have addressed that chemically functionalized Si surfaces are promising solutions.

In this work, Copper (hexafluoroacetylacetonato) vinyltrimethylsilane, or Cu(hfac)VTMS, was used to deposit copper nanoparticles on several functionalized Si surfaces including H-Si(100), H-Si(111), NH₂-Si(100),

NH-Si(100), NH_x-Si(100), and OH-Si(100). With atomic force microscopy (AFM), infrared spectroscopy (MIR-FTIR), X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD) supported with density functional theory calculations (DFT), we have investigated the reaction kinetics and mechanism of the surface reaction and the effects of Si surface functionalization on particle size control and elemental composition of the as-deposited film.

AS-TuP21 Dry Cleaning Methods for Single Reconstructions of (100) InGaAs Following Air Exposure and Post Annealing Conditions, W. Melitz, M. Edmonds, T.J. Kent, A.C. Kummel, University of California San Diego

In effort to further reduce the EOT scaling process while simultaneously maintaining low Dit and high mobility on III-V semiconductor surfaces, dry cleaning methods have been implemented to help create uniform and ordered semiconductor surfaces. The scaling of gate oxides on MOSFETs requires ALD oxide nucleation in every unit cell of the semiconductor channel surface, a process which depends having a highly ordered semiconductor with the minimization of surface defect sites which prevent ALD oxide deposition thereby inducing pihole formation. Through the use of in situ scanning tunneling microscopy (STM) and an atomic hydrogen cleaning technique, air exposed (001) InGaAs samples with an In/Ga rich 4x2 surface reconstruction and an As rich 2x4 surface have been restored to the order and cleanliness of MBE grown samples.

The InGaAs samples were exposed to air, containing NO_x, ozone, and hydrocarbons, and returned to UHV for STM atomic imaging. Imaging confirmed the surfaces became amorphous upon air exposure. The samples were exposed to 150L dose of atomic hydrogen at 380°C. After atomic hydrogen dosing, STM revealed the restoration of the ordered pure In/Ga rich 4x2 surface reconstruction with highly flat atomic terraces. Atomic H cleaning results in formation of deep etch features but a subsequent anneal at 460 °C for 30 min can reduce this effect. Etch pit density has been quantified for samples both after hydrogen dosing and after the post annealing process. Results showed a 98% reduction in etch pit density following the post annealing process [1]. For formation of the pure As-rich 2x4 reconstruction with no group III rich regions, a relatively small processing window was found introducing the air exposed sample to a 1800L dose of atomic hydrogen at 285°C to form the pure 2x4 reconstruction. Etch pit formation occurred following hydrogen dosing and the samples were subsequently annealed to 290°C for 30 minutes. Etch pit density was quantified for samples before and after post deposition annealing and results showed a decrease in etch pit density by 55% following the post annealing process.

[1] W. Melitz, J. Shen, T. Kent, A. C. Kummel, and R. Droopad, " InGaAs surface preparation for ALD by hydrogen cleaning and improvement with high temperature anneal," *J. Appl. Phys.*, vol. 110, p. 013713, 2011.

AS-TuP22 The Effect of Gas Environment on the Electronic and Optical Properties of Amorphous Indium Zinc Tin Oxide Thin Films, Y.R. Denny, S.Y. Lee, K.I. Lee, S.J. Seo, Chungbuk National University (CBNU), Republic of Korea, S. Heo, J.G. Chung, J.C. Lee, Samsung Advanced Institute of Technology, Republic of Korea, H.J. Kang, Chungbuk National University (CBNU), Republic of Korea

The electronic and optical properties of Indium Zinc Tin Oxide (IZTO) thin films were investigated by X-ray photoelectron spectroscopy (XPS) and reflection electron energy loss spectroscopy (REELS). IZTO thin films on a glass substrate have been prepared by RF magnetron sputtering. The composition ratios of In:Zn:Sn in IZTO thin films are 20:56.7:23.3. The films were deposited at the annealing temperature of 350 °C for 1 hour in air, oxygen mixed with water (annealed at 350°C), and 80% oxygen mixed with argon (without annealing). The XPS spectra shows that all IZTO thin films have the Sn-O, In-O, and Zn-O bonds. The REELS spectra revealed that the band gaps of IZTO thin films are 3.23 and 3.07 eV for water mixed oxygen and argon mixed oxygen, respectively. The value of band gap increased to 3.46 eV when the sample was annealed in air. All the measured band gaps by REEL are consistent with the optical band gaps determined by UV-Spectrometer. The average optical transmittance of all IZTO thin films in the visible light region was 86%. The sheet resistivity of IZTO thin films deposited in water and argon mixed oxygen was 5 times lower than that of air, which indicates that gas environment plays an important role in increasing the figure of merit (ϕ_{TC}) and thus improving the electrical and optical properties of IZTO thin films.

AS-TuP23 Modification of Metal – InGaAs Schottky Barrier Height by Atomic Layer Deposition of Ultrathin Al₂O₃ Interlayers. *L. Chauhan*, Dublin City University, Ireland, *S. Gupta, P. Jaiswal, N. Bhat, S.A. Shivashankar*, Indian Institute of Science Bangalore, India, *G.J. Hughes*, Dublin City University, Ireland

High indium content InGaAs is a leading candidate for n-channel devices in future generations of complementary metal-oxide-semiconductor (CMOS) technology due to its high electron mobility and high saturation velocity. In recent years significant progress has been made in improving the electrical quality of the high-k dielectric InGaAs interface by the atomic layer deposition (ALD) of high-k materials on passivated surfaces. An additional technological issue which needs to be addressed for metal oxide semiconductor field effect transistors (MOSFETs) fabrication is the relatively high source/drain (S/D) contact resistance which results from poor dopant activation in III-V semiconductors. One proposed solution to this issue is to fabricate metal S/D Schottky-barrier MOSFET devices which requires control over the barrier height at the metal-InGaAs interface. It has recently been reported that the insertion of an ultrathin layer dielectric layer at the contact interface between the metal and the semiconductor can help in releasing the Fermi level to obtain a rectifying contact.

In this study we investigate the effectiveness of the insertion of an ultrathin ALD deposited Al₂O₃ dielectric layer on the Schottky barrier formed at the interface between the metal and the InGaAs. Schottky contacts were fabricated on 1nm and 2nm Al₂O₃ layers deposited on native oxide and sulphur passivated In_{0.53}Ga_{0.47}As for both n and p doped substrates. To investigate the dependence of Schottky barrier height (SBH) on metal work function (WF), both low (Al~4.30 eV) and high (Pt~5.65 eV) WF metals were deposited on these surface.

Rectifying behaviour was observed for the p-type substrates for the Al-InGaAs and Al/Al₂O₃/InGaAs junctions and the SBH was measured to be ~0.60eV. Ohmic behaviour was observed on the Pt-InGaAs and Pt-Al₂O₃-InGaAs junctions regardless of the dielectric thickness. The Al₂O₃/InGaAs interfacial chemistry of these surfaces was investigated with x-ray photoelectron spectroscopy and no arsenic oxide was found on the Al₂O₃-native and sulphur treated InGaAs surfaces which suggests that on the native oxide InGaAs surface, Al₂O₃ deposition resulted in the consumption of the interfacial oxide.

Ohmic behaviour was observed on the all n-type metal/InGaAs and metal/Al₂O₃/InGaAs junctions regardless of the metal WF or thickness of the dielectric layer which suggests that the Fermi level is pinned near to the top of the conduction band for these InGaAs samples.

AS-TuP26 STM Imaging and Manipulation of a Three-Metal-Center Organometallic Molecule. *N.A. Wasio, R.C. Quardokus, Y. Lu, S.A. Kandel*, University of Notre Dame

The electronic properties of a trimetallic molecule, [$\{Cp^*(dppe)Fe(C\equiv C)\}_3(1,3,5-C_6H_3)\}$] (**Fe3**), are characterized to explore potential uses of these molecules in molecular-electronic devices. Scanning tunneling microscopy (STM) at 77 K under ultra-high vacuum is used to study the adsorption of **Fe3** on the Au(111) surface. Neutral **Fe3** and mixed-valence species (**Fe3⁺** and **Fe3²⁺**) are investigated, and STM images are shown to be sensitive to the intramolecular distribution of charge. Experimental data are compared to simulated theoretical results and tip-molecule manipulation is also explored.

AS-TuP27 Development of Advanced SIMS Single Stage Accelerator Mass Spectrometer Instrument at the Naval Research Laboratory. *K. Fazel, K. Grabowski, D. Knies, G. Hubler*, Naval Research Laboratory

The Naval Research Laboratory (NRL) will be constructing a SIMS Single Stage Accelerator Mass Spectrometer (SSAMS) instrument starting at the end of 2013 for use with nuclear forensics, cosmology, and other applications. The instrument will enable analysis of both positive and negative ions, and will have a molecular destruction capability. These features will address our goal to improve sensitivity and precision of select species, broaden the range of elements and isotopes to measure, and ease sample chemical pre-processing requirements.

To provide these features, the front portion of a Cameca IMS 6f will be combined with an NEC SSAMS system. The NEC SSAMS system will include a bipolar 300-kV air insulated single stage accelerator, custom multi-port 90° high mass resolution injection magnet ($ME/Z^2 = 2.6$ amu-MeV), 90° double focusing analysis magnet ($ME/Z^2 = 75$ amu-MeV), electrostatic spherical analyzer, and a molecular ion dissociator. High-speed electrostatic switching is also included in both magnets to allow high efficiency and precision of measurements of small sample particles. The multi-port injector magnet enables nearly continuous matrix normalization over a large mass range without having to change the magnetic field of the injector. The bipolar power supply for the accelerator allows measurement of both electropositive and electronegative elements, while the molecule destruction feature minimizes molecular interferences. Access to

electropositive elements should provide improved sensitivity for rare earth elements, Uranium, and Plutonium. Before NRL can apply the instrument, the fundamentals of the instrument must be established.

The fundamentals include establishing molecular destruction cross sections of anticipated molecular ions, charge state distributions, overall transmission, and molecule fragment patterns. Upon establishing the performance characteristics of the instrument, the NRL SIMS-SSAMS will be unique tool able to better understand the constituents of an unknown material in nuclear forensics, cosmology, and other applications.

AS-TuP28 Catalytic Effect of Ni in the Gasification of Flexicoke with Water Steam. *J.C. De Jesus, I.J. Gonzalez*, PDVSA Intevep, Venezuela (Bolivarian Republic of), *E.A. Rendon*, Universidad Central de Venezuela, (Bolivarian Republic of)

In Venezuela, the hydrocarbon refining industry produces approximately 400 TPD of flexicoke, a by-product of the FlexicokingTM process, a technology that thermally transforms heavy oils to lighter more valuable products. This solid material concentrates large amounts of vanadium and nickel, and it is usually traded for power generation or metal recovery. However, the indigenous metals in this carbonaceous solid present inherently an excellent dispersion and therefore some potential for complementary catalytic applications. For solid carbonaceous feedstocks, V has been reported to enhance combustion while Ni has shown a good activity to promote gasification with steam for the generation of valuable synthesis gas. However, most conclusions have been extracted from experiences at laboratory scale with synthetic samples, and not with real world ones collected from commercial plants. In this contribution, a real flexicoke sample obtained from a refinery is lixiviated with base and acid to allow the selective removal of each metal, and the assessment of the activity of the individual elements towards the promising gasification with steam is monitored in a thermogravimetric analyzer coupled to a quadrupole mass spectrometer for evolved gas analysis. Analysis by XPS permits the correlation of surface metal composition with catalytic activity monitored during the course of the test reaction. It is shown that Ni catalytically enhances the conversion of the flexicoke to CO and H₂ at a temperature much lower than the one observed thermally both in the original sample and in the fully demetalized carbon matrix. In addition, Ni activity is inhibited in the presence of V, presumably due to the formation of a deactivating layer on top of the Ni surface and, therefore, V must be selectively removed from the original material for the catalysis to take place.

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