Tuesday Afternoon Poster Sessions

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

Applied Surface Science Poster Session

AS-TuP1 Application of an Electrospray Technique to Secondary Ion Mass Spectrometry (SIMS)*, Y. Fujiwara, N. Saito, H. Nonaka, T. Nakanaga, S. Ichimura*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

An electrospray technique can generate a continuous stream of charged droplets at currents exceeding 1000 nA. We expect that it has a great potential in Secondary Ion Mass Spectrometry (SIMS). Consequently, we investigated beam generation characteristics using the electrospray technique operated at atmospheric pressure and under reduced pressure (i.e., vacuum).

When electrospraying is performed at atmospheric pressure or above, emitted charged droplets and ions are required to be sampled through an aperture into a vacuum chamber, and then accelerated toward a target. It was confirmed that a beam current was considerably reduced in the process passing through the aperture; for instance, passing efficiency through the 120-mm aperture was on the order of 10^{-3}. This loss mainly results from the spreading of electrosprayed ions at atmospheric pressure.

When electrospraying is done in a vacuum, freeze and evaporation of a solution will be a serious problem. In other words, in the case of frequently-used solutions such as water and ethanol, it is difficult to achieve stable electrospraying in a vacuum because of the freeze and evaporation around a capillary tip. To solve the problem, we have proposed a vacuum electrospray beam source using pure ionic liquids for SIMS application. Ionic liquids have very low vapor pressure as well as high ionic conductivity; its use will enable us to perform stable electrospraying in a vacuum. We investigated the electrospray characteristics of an ionic liquid in a high vacuum environment with pressures around 10^{-5} Pa using the stainless-steel capillary. The experimental results demonstrated that stable electrosprayed currents of the order of 1000 nA can be continuously generated in both positive and negative modes. Experimental results indicate that the electrospray technique seems to be applicable to SIMS.

AS-TuP2 Structure and Chemical Composition of Thiol-SAMs on Au Surfaces for Biological Applications*, M. Bruns, S. Engin, V. Trouillet, D. Wedlich*, Karlsruhe Institute of Technology, Germany*, P. Brüner, T. Grehl, S. Kayser*, ION-TOF GmbH, Germany*, P. Mack, R.G. White*, ThermoFisher Scientific, UK

Structured and oriented immobilization of bio-molecules has become subject of great interest in recent years due to the expected diversity of applications, e.g. bio sensors in diagnosis, lab-on-chip technology, and modern cell culture focused on cell adhesion, migration, and differentiation. Therefore, a lot of effort has been spent to develop strategies for covalent and non-covalent immobilization of proteins, respectively. A very promising approach is surface patterning by micro-contact printing (μCP) to produce self-assembled-monolayers (SAMs) on gold surfaces based on mixtures of benzylguanine thiol (BGT) and matrix thiol. In this case BGT is the substrate for the SNAP-tag system, allowing for covalent attachment of any protein of interest fused to this tag, whereas the inert matrix thiol acts as spacer for BGT and moreover prevents from non-specific protein adsorption.1

The present contribution focuses on the characterization of pure benzylguanine and matrix thiols as well as mixtures of both using a combination of complementary surface analytical methods. For this purpose all SAMs were prepared on gold films deposited onto glass substrates by r. f. magnetron sputtering directly prior to the thiol exposure. The chemical composition and the covalent binding of the thiols were proved by time-of-flight secondary ion mass spectrometry (ToFSIMS) and X-ray photoelectron spectroscopy (XPS) as well. The orientation of the SAMs together with thickness information were achieved by high-sensitive low-energy ion scattering (LEIS),2and were justified by non-destructive depth profiles reconstructed from parallel angle-resolved XPS data applying a maximum entropy algorithm. Finally the μCP micro-structures were verified by ToFSIMS.

S. Engin, V. Trouillet, C. M. Franz, A. Welle, M. Bruns, and D. Wedlich, *Benzylguanine Thiol Self-Assembled Monolayers for Immobilization of SNAP-tag Proteins on Microcontact printed Surface Structures*, Langmuir, DOI: 10.1021/la904829y.

H. H. Brongersma, Th. Grehl, P. A. van Hal, N. C. W. Kuijpers, S. G. J. Mathijssen, E. R. Schofield, R. A.P. Smith, H. R.J. ter Veen, *High-sensitivity and high-resolution low-energy ion scattering*, Vacuum **84** (2010) 1005-7.

AS-TuP3 Thickness and Composition of the HfO2/Si Interface Layer As a Function of Aperture-Time of Oxidant-Agent for ALD-grown HfO2 Nanofilms*, P.G. Mani-Gonzalez, M.O. Vazquez-Lepe, A. Herrera-Gomez*, CINVESTAV Queretaro, Mexico

Hafnium oxide nanofilms were grown with ALD (Atomic Layer Deposition) on H-terminated Si(001) wafers employing TDMA-Hf (tetrakis dimetil animo hafnium) and water as precursors. The structure of the films was characterized with angle-resolved X-ray photoelectron spectroscopy (ARXPS). While the aperture-time for TDMA-Hf was kept constant at 0.08 s during the ALD deposition, the aperture-time (t H2O) for the oxidant-agent (H2O) was varied from 0 to 0.1 s among the different samples. The water exposition-time has a direct effect on the thickness of the HfO2 layer, which saturates at ~ 1.7 nm for 30-cycle ALD processes. The composition and thickness of the interface between Si and hafnia is approximately constant at Hf0.5Si0.5O2 and 1 nm for 0.02 < t H2O <0.06 s. For larger aperture-times, the Hf contribution to the composition rises slowly; the thickness of the layer also rises slowly. The total film thickness, including the hafnium silicate and hafnium oxide layers, saturates at ~ 3 nm. Our results are in accordance with prior results, which estimate the film growth rate at ~ 1 Å per ALD cycle.

AS-TuP4 Defect States in Amorphous GaInZnO Thin Film Grown on SiO₂/Si Substrates*, S. Heo, J.G. Chung, H.I. Lee, E.H. Lee, J.C. Lee, G.S. Park,* Samsung Advanced Institute of Technology, Korea*, J.S. Oh, H.Y. Cho,* Dongguk University, Korea*, D. Tahi, L.S. Son, S.K. Oh, H.J. Kang,* Chungbuk National University, Korea*, T. Nagatomi, Y. Takai*, Osaka University, Japan

Transparent oxide conductor and semiconductor are useful for us to develop electronic components in various applications such as flat panel display and solar cells. In particular, amorphous Ga-In-Zn-O (a-GIZO) thin films are promising channel materials for thin film transistors (TFTs) because a-GIZO TFTs exhibit large field-effect mobility (>10 cm2/V s) irrespective of their fabrication on various substrates, such as silicon, glass, plastic, polyimide, polyethylene terephthalate (PET), cellulose paper and flexible substrates. In addition, they have superior uniformity, low processing temperature, possibility of large-area deposition and long term stability, and moreover they are cost effective.

In recent years, a large progress has been made in high performance TFTs based on a-GIZO as channel layers. Amorphous semiconductors have defect states originating from structural disorder and defect, which strongly affect carrier transport properties and devices performances. However, fundamental material properties of a-GIZO such as the band alignment and defect states, which are important for devices structure and circuit configuration have not been investigated in detail so far. Moreover, any investigation of band alignment and defect states of a-GIZO thin films is very important to understand the transport mechanism and to improve device performances.

In this study, we have investigated the band gap, valence band offset and defect states of GIZO thin films by using reflection electron energy loss spectroscopy (REELS), X-ray photoelectron spectroscopy (XPS), thermally stimulated exo-electron emission (TSEE) and photoinduced current transient spectroscopy (PICT). The band gap and valence band offset (VBO or ΔE_V) allow us to determine the conduction band offset ΔE_C by using the relation: $\Delta E_C = E_g(SiO2) - \Delta E_V (GIZO/SiO2/Si) - E_g(a\text{-}GIZO)$. The band gap is 3.2eV, and the conduction band offset of GIZO is 3.62 eV. The shallow defect states obtained via PICT were at 0.24eV and 0.53eV below the conduction band minimum of a-GIZO thin film, and the deep defect state obtained by means of TSEE is 1.827eV below the conduction band minimum of GIZO thin film.

AS-TuP5 Band Alignment and Defect States in Amorphous Si-N Compounds on Si Substrates*, H.I. Lee*, Samsung Advanced Institute of Technology

Silicon nitride (SiN$_x$) has an important application in the photovoltaics. First, plasma SiN films have provided effective surface passivation of silicon solar cells. Secondly, SiN has an important application in electronic memory devices. The memory property of the amorphous silicon nitride (a-SiN$_x$) is due to its electronic structure dominated by many deep traps.

Electronic properties of a-Si₃N₄ are determined mainly by deep traps of electrons and holes as well as by hollow traps responsible for the spreading of charges captured by deep traps. In other words, they are responsible for the degradation of nonvolatile memory devices based on NMOS. Because of this, a correct knowledge about the nature of levels is extremely

important in selecting the technology for the preparation of layers intended for specific application.

In this study, in order to obtain band alignment as well as defect state of SiN_x thin films, we have investigated the band gap and valence band offset with the variation in the composition of N contents by using reflection electron energy loss spectroscopy (REELS) and X-ray photoelectron spectroscopy (XPS), respectively. The defect states were investigated by using thermally stimulated exo-electron emission (TSEE), which have been specially designed for in-situ measurement of a defect state in analysis chamber without any electrodes.

Our result shows that the valance band offsets were increased from 0.033 eV to 1.24 eV with increasing N contents. The band gap was changed from 3.2 eV to 4.7 eV for the above materials. The defect state energy of the a-SiN_x films were observed at 1.85 eV by using thermally stimulated exo-electron emission. This energy is related to hydrogen migration or a dangling bond ($\cdot Si\equiv$), called the K center, in the silicon nitride.[1] The values of deep trap energy below the conduction band are independent of N content.[2] The defect state energy are properly assigned.

AS-TuP6   X-ray Degradation of Oxygen Plasma Treated and Chemically Reduced Poly(propylene) Surfaces in Comparison to Conventional Polymers, *T. Gross*, BAM Federal Institute for Materials Research and Testing, *W.E.S. Unger, G. Kühn*, BAM Federal Institute for Materials Research and Testing, Germany

X-ray induced sample damage during mono XPS analysis of an oxygen plasma oxidized and subsequently wet-chemically reduced poly(propylene) film was investigated as a example for plasma modified or plasma deposited samples. By doing this the degradation index approach as introduced by Beamson and Briggs in the Scienta ESCA300 high resolution XPS data base of organic polymers has been adopted. As to be expected the sample degrades by loosing oxygen as revealed by observation of decreasing O/C and C-OR/Csum ratios. However, the X-ray degradation indices are definitely higher than those of conventional reference polymers. Moreover, the C-OR/Csum degradation index is significantly higher in comparison to this one obtained for the O/C ratio. In that context there is no difference between the plasma sample and a conventional poly(vinyl alcohol) polymer. It is concluded that for reliable quantitative surface chemical analysis the quality of spectra in terms of acquisition times must be optimized aimed to a minimization of X-ray degradation. Finally it is proposed to describe the photon flux of a X-ray gun in an XPS experiment, which defines the degradation rate at the end, by using the sample current simply measured with a carefully grounded sputter-cleaned reference silver sample.

AS-TuP7   Analysis of Friction and Wear Mechanisms on Hard Coatings Deposited by Reactive Magnetron Sputtering, *J.S. Restrepo*, Universidad Autonoma de México, *M.F. Cano, J.M. Gonzalez, A. Ruden, F. Sequeda*, Universidad del Valle, Colombia

Different Hard coatings have been deposited (ZrN, CrN, TiN, TiZrN, TiAlN, AlSiN and multilayers systems) by DC Reactive Magnetron Sputtering at different deposition parameters (substrate temperature, Nitrogen flow, Voltage bias), to evaluate tribological properties with a ball on disc technique using different loads and speeds parameters to know the influence of this, on the tribological behavior. The ball on disc test was stopped at different distances to identify the wear mechanisms using a profilometer, scanning electron microscopy (SEM) and optical microscopy. These techniques allowed observed differents transitions on friction coefficient associated with the wear mechanisms. The rugosity polishing showed a low friction coefficient that increases slowly, the ploughing and scratching wear mechanisms were observed, producing unstable high friction coefficient and wear rate. Also different kinds of debris particles were observed like angular and roll shape.

AS-TuP8   Tribological and Mechanical Properties of Multilayer TiN/Cr_xN Coatings Deposited by Reactive Magnetron Sputtering, *F. Correa*, Universidad Autonoma de Occidente, Colombia, *M.F. Cano, J.M. Gonzalez, A. Ruden*, Universidad del Valle, Colombia, *J.S. Restrepo*, Universidad Autonoma de Mexico, *F. Sequeda*, Universidad del Valle, Colombia

AS-TuP9 Multi-scale Characterization Studies of Li-ion Batteries, *S. Nagpure, B. Bhushan, S. Babu, G. Rizzoni*, The Ohio State University

Advanced Li-ion batteries with high energy and power density are fast approaching compatibility with automotive demands. While the mechanism of the operation of these batteries is well understood the aging mechanisms are still under investigation. While aging at the macroscopic level is directly measurable by increase in the internal resistance, at material level that include cathode, anode, separator and electrolyte aging can be attributed to many degradation mechanisms. As, the degradation of the material is caused by several simultaneous physiochemical processes that occur within the batteries, material characterization in automotive application batteries is a challenging task. We have identified and tested a set of experimental techniques for multi-scale characterization of the cathode in the Li-ion batteries. The electrical properties are studied using the electrochemical impedance spectroscopy and scanning spreading resistance microscopy. The structural degradation is studied using the infrared thermal imaging (meters), scanning electron microscope (micro), X-ray diffraction (micro), atomic force microscope (micro to nano), transmission electron microscope (micro) and electron energy loss spectroscopy. Finally, a relatively new neutron depth profiling technique was successfully used in these studies to study the transport and concentration of lithium within the few microns of the cathode thickness. We present the results obtained from this set of experiments when applied to the samples extracted from an unaged and an aged $LiFePO_4$ based Li-ion battery.

AS-TuP10   Improved Tougaard Background Calculation using Predetermined Inelastic Electron Scattering Cross Section Functions K(T) using the Software UNIFIT 2011, *R. Hesse, R. Denecke*, Universität Leipzig, Germany

The shape of the background in x-ray photoemission spectra may be affected by secondary electrons and inelastic energy loss processes. A polynomial of low order has very often turned out to model the secondary electron background. The Tougaard background model [1] has been successfully used to characterise the inelastic loss processes. However, the correct usage of the Tougaard background needs a well defined K(T) function (T = energy loss). The introduction of a four parameter loss function K(T) = BT/(C-C'T²)²+DT² with the fitting parameters B, C, C' and D implemented in the fittable background function [2] allows the improved estimation of the K(T) function. The results will be compared with the recommended parameters by Tougaard. The calculation of inelastic electron scattering cross sections of clean surfaces from different materials using UNIFIT will be demonstrated.

[1] S. Tougaard, Surf. Interface Anal. 25 (1997) 137

[2] R. Hesse, T. Chassé, R. Szargan, Fresenius J. Anal. Chem., 365 (1999) 48

AS-TuP11   Comparative Study of Two Different Methods for Film Thickness Determination on Model and Real Systems using the Software UNIFIT 2010, *R. Hesse, P. Streubel, R. Denecke*, Universität Leipzig, Germany

The accuracy of thickness determination of laterally homogenous films by XPS in the range of few nm may be improved by combining two different methods. The results of the well established angle resolved photoelectron spectroscopy (**ARXPS**) for determining film thicknesses will be compared with the ones determined using the relative quantification of photoelectron lines at two different kinetic energies (i.e. energy-resolved) and the same emission angle (**ERXPS**). Only the substrate intensities were used. The advantages and disadvantages of both methods will be shown. The reliability and accuracy of the thickness determination by the two different methods is discussed for suitable model and real systems. The easy handling of the data analysis for estimating film thicknesses using UNIFIT will be demonstrated.

AS-TuP12 Non-destructive In-Depth Chemical Characterization of Air Exposed Plasma Polymers by Energy Resolved XPS, *P.-L. Girard-Lauriault, I. Retzko, S. Swaraj*, BAM Federal Institute for Materials Research and Testing, Germany, *N. Matsubayashi*, National Institute of Advanced Industrial Science and Technology (AIST), Japan, *T. Gross, W.E.S. Unger*, BAM Federal Institute for Materials Research and Testing, Germany

Plasma polymers can be deposited on a wide range of substrates in order to introduce a desired surface chemistry intended for a wide range of applications. For many of these, only the chemistry of the outermost surface layer is relevant and therefore, many works have favoured the use of surface-specific techniques such as X-ray photoelectron spectroscopy (XPS) or time of flight secondary ion mass spectrometry (ToF-SIMS), which have various sampling depth under the surface. Recently, a technique enabling XPS depth resolution by the modulation of the photoelectron attenuation length for non-destructive chemical depth profiling, known as energy-resolved XPS (ERXPS), has emerged. In the best case, the minimum attainable 95 % information depth value is about 22 % of its value under standard Al Kα XPS conditions, thus permitting a better surface sensitivity than angle resolved XPS (ARXPS). ERXPS has also many other positive points that are thoroughly discussed.

In this study, plasma polymers containing oxygen and nitrogen based surface chemistries were prepared from allylalcohol, allylamine and acrylic acid. Established selective chemical derivatisation procedures with trifluoroacetic anhydride (TFAA) and 4-trifluoromethyl benzaldehyde (TFBA), are used to determine alcohols and amines, respectively. All

samples were analysed by energy resolved XPS (ERXPS). By analysing the high resolution spectra we demonstrate that slightly aged plasma polymers prepared from allylalcohol and allylamine present a homogeneous in-depth chemistry in the range of XPS information depth (≈10 nm) while this was clearly not the case for their acrylic acid counterparts. Furthermore, it is shown that standard derivatisation reactions result in homogeneous changes of the chemistry in the above-mentioned information depth.

AS-TuP13 , *V. Smentkowski*, GE Global Research Center, *M.R. Keenan*, Consultant

Depth profiling via ToF-SIMS is a well established technique that is used to determine the depth distribution of trace species in samples. 3D depth profiling techniques are now being heavily utilized in the ToF-SIMS community since it enables the measurement of both the depth distribution and the lateral distribution of the species. 3D ToF-SIMS analysis are revealing that many samples are not uniform in the lateral dimension. Since a full mass spectrum is saved at every volume element, unexpected species are often found sub-surface, especially in real-world sample. Unfortunately, one often needs to perform two depth profile measurements in order to fully characterize a sample – a positive ion measurement to look for electropositive species with the highest sensitivity and a negative ion measurement in order to analyze electronegative species with the highest sensitivity. The two depth profile measurements are often performed using different erosion sources and experimental conditions which have been optimized for the species to be analyzed and often have significant differences in the erosion rate. Since the analysis are performed in two different regions of the sample, one can not correlate species observed in the two independent measurements. Additionally, there are instances where the amount of material is limited and one can not perform two measurements. MCs^+ analysis have been reported in the ToF-SIMS literature. For MCs^+ analysis one uses a Cs^+ ion beam to erode the sample, and a Bi_3^+ ion beam to perform the analysis in the positive ion polarity. Electropositive species are detected as M^+ and/or $M+Cs^+$ and the electronegative species are detected as M^+ and/or $M+Cs2^+$ (where M is the element being analyzed). In this paper, we will demonstrate, for the first time, the ability to analyze complicated 3D MCs^+ ToF-SIMS data sets using MVSA techniques. We will show the advantages of MVSA analysis over univariate analysis.

AS-TuP14 Metal Silicide Nanoscale Chemical Characterization with Scanning Auger Microscopy, *D.F. Paul*, *J.S. Hammond, D.G. Watson*, Physical Electronics

Scanning Auger Microscopy is a powerful compositional analysis technique for surfaces and nanostructures. It is well known that Auger instruments based on full CMA analyzers provide a stable imaging platform and analytical capability that can be successfully applied to a wide range of material systems. Recently a high energy resolution spectroscopy mode that provides enhanced chemical characterization was added to a CMA Auger instrument. This new functionality is integrated with the instrument while maintaining all the existing capabilities and benefits associated with the CMA based Auger instrument.

The usefulness of this new high energy resolution spectroscopy mode will be demonstrated with detailed chemical information from annealed metal silicide ultra thin films on silicon wafers. Low energy ion beam depth profiling facilitates a chemical state evaluation of the silicide/wafer interface induced by the annealing process. Auger mapping and high energy resolution Auger spectroscopy also characterizes the three dimensional nanostructures formed on the surface and at the interfaces of these metal silicide ultra thin films.

AS-TuP15 Influences Finish Quality in Machining Austempered Ductile Iron, *W. Mattes*, SENAI-SC, Brazil, *A.C. Bottene*, LOPF/NUMA, Brazil, *R. da Silva*, UNERJ, Brazil

The austempered cast iron (ADI - Austempered Ductile Iron), has been successfully applied in diesel trucks, class 8 trucks and agricultural tractors power train parts. This material has also been used in high performance gears, applied in various segments of the mechanical industry, especially in the automotive field because of their properties and technical advantages associated to the combination of strength and ductility of the material. The main technical limitation of the ADI is attributed to its machinability. This problem is related to the hardening that occurs by the transformation of austenite, characteristic of the microstructure of austempered ductile, which affects the steps of the production process and achieve common cropping the part before the heat treatment and finish machining right after them. This paper discusses a study on the behavior of the surface finish quality, technical and financial feasibility of the machining process. Comparing the use of grinding, CBN wheel, and the hard turning operation, cemented carbide coated TiAlCrN, of ADI by comparative analysis of lifetime of the

tools in terms of speed of cutting, using as a criterion to end the life of the tool flank wear of 0.3 mm.

AS-TuP17 Tougaard Background Parameters - Simpler Than One Might Expect, *P.J. Cumpson*, Newcastle University, UK

Several methods of calculating - or subracting - inelastic backgrounds from XPS spectra have been published over the years. Perhaps the most successful for practical XPS analysis has been the Tougaard background[1,2]. Tougaard proposed Universal Backgrounds that apply to most materials of analytical interest, yet are determined by only three or four parameters. In principle this allows the automatic removal of a large proportion of the inelatstic backround in many cases, but in practice there is often a problem in selecting appropriate Tougaard background parameters. These parameters do not have immediate physical interpretations, and it is often difficult to see which values are physically possible and which are not. Therefore it seems difficult, for example, to include all four of these parameters in a fit to an experimental spectrum; the fit would be ill-conditioned and underdetermined. The problem is made worse by the necessarily narrow energy ranges of backgrounds available for background fitting in practical applications.

We show that there are significant relationships between the four parameters in the Tougaard model, and connect these with materials parameters. The result is a background that depends upon a single parameter that can be included in a least-squares fit to any practical multi-element spectrum.

[1]. S. Tougaard og I. Chorkendorff, Differential Inelastic-Electron Scattering Cross Sections from Experimental Reflection-Electron Energy-Loss Spectra: Application to Background Removal in Electron Spectroscopy. Phys. Rev. B35, 6570 (1987).

[2] S. Tougaard, Universitality Classes of Inelastic Electron Scattering Cross Sections. Surface Interface Analysis, Vol 25, 137-155 (1997).

AS-TuP18 XPS Analysis of Surface Films Formed on Common Metals on Exposure to Ethanol-Blended Fuels, *H.M. Meyer III, S.J. Pawel*, Oak Ridge National Laboratory

Most automobile fuels contain some amount of ethanol, typically around 10% by volume, and fuels with higher ethanol levels are available. In Brazil mandated ethanol levels are 25% (E25 fuel) and in 2009 over 9 million vehicles were on the road using pure ethanol (E100) as fuel. Certainly, in the years ahead increasing levels of ethanol will be available in US fuels. As such, most automobile manufacturers are producing engines that can handle a variety of ethanol-blends. This poster examines several common metals used in fuel storage and fuel handing equipment, namely brass, galvanized steel, and nickel, and compares unexposed material to material that has been exposed to (1) reference gasoline and (2) E10 fuel and (3) E25 fuel. Samples were cleaned (acetone + ultrasonic), weighed, and placed in a stainless steel vessel. Fuel was added and the vessel was purged with Ar and sealed. After raising the temperature to 60 C, the samples were left for 28 days. Upon removal, the samples were rinsed with pure ethanol, dried, and weighed. X-ray photoelectron spectroscopy was used for determining surface composition. Sputter profiling was used to monitor changes in composition as a function of depth. For some samples, XPS mapping was employed to determine lateral distribution of chemical species. Results presented in this poster clearly show greater oxidation and the formation of metal sulfide species for the ethanol-blended fuels as compared to the reference gasoline. Increasing the ethanol content above E10 to E17 showed an increase in the extent of oxidation and formation of metal sulfides.

AS-TuP19 Sputtering of Lunar Regolith Simulant by Singly and Multicharged Constituents of the Solar Wind, *F.W. Meyer, P.R. Harris, H.M. Meyer III*, Oak Ridge National Laboratory, *N. Barghouty, J.H. Adams, Jr.*, Marshall Space Flight Center NASA

We report preliminary results on sputtering of a lunar regolith simulant sample by H^+, Ar^+, Ar^{6+} and Ar^{9+} at solar wind-relevant energies. Such interactions are an important determinant of lunar exosphere composition, and may provide a possible pathway leading to the production of water on the moon. The presence of lunar water was recently confirmed by a number of orbiting lunar missions. The ions are generated using an electron cyclotron resonance (ECR) ion source at source potentials between 10-15kV. After being extracted, transported, and decelerated, the ions are normally incident on a pressed lunar regolith simulant sample that is situated within a floating UHV scattering chamber. The relative bias between the ECR source and the surface end station was adjusted to produce a constant impact energy of 0.375keV/amu for each of the 4 ion beams investigated. To simulate the effect of the dominant proton component, which constitutes >90% of the solar wind, the lunar regolith simulant sample was prepared by exposure to a proton beam up to total

fluences of $\sim 2 \times 10^{18}$ H$^+$/cm^2 prior to each of the Ar beam sputtering runs. Both transient and steady state conditions of sputtered species were monitored by a quadrupole mass spectrometer situated within the UHV scattering chamber. SEM and XPS analyses of the JSC-1A AGGL simulant were performed to monitor possible changes in surface morphology and composition during the pressing of the loose powder into the sample holder.

AS-TuP20   Chemical Depth Profiling: Relating Interfacial and Sub-surface Characterization to Electrical Performance, *K.G. Lloyd, L. Zhang, J.P. Wyre, J.R. Marsh, M.A. Plummer*, DuPont Corporate Center for Analytical Sciences

Thin multi-layered structures form the basis for photovoltaic/solar cells, OLED displays, and many other electronic devices. Electrical performance can be influenced by the thickness of these layers, the widths of interfaces between layers and/or development of interfacial chemistry, and the extent and location of dopants within layers. Depth profiling, i.e., obtaining chemical information as a function of dpeth, can provide this information, especially for systems wehre cross-sectioning is not an option, species of interest are present below 1%, or sampling with better than 1 micron depth resolution is required.

ToF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry) and X-ray Photoelectron Spectroscopy (XPS, a.k.a. ESCA) are typically used in conjunction with a high-current ion sputter beam to analyze the outermost surfaces as they are freshly revealed. ToF-SIMS depth profiling offers high mass resolution, spatially-resolved chemical information, and the collection of the entire mass spectrum at each depth interval. The combination of ToF-SIMS depth profiling and multivariate methods of data analysis allows better definition and characterization of interfacial regions between layers.

Examples include characterization of the BSF (back surface field) layer on solar cell backsides, monitoring layered oxide growth on annealed stainless steels, and study of interdiffusion in organic electronic layered structures.

AS-TuP21   In-situ XPS Analysis of Co and Co^{2+} during Steam Reforming of Ethanol on Supported Cobalt Catalysts, *A. Karim, Y. Su, M.H. Engelhard, D. King, Y. Wang*, Pacific Northwest National Laboratory

In catalysis, the oxidation state of metal nanoparticles on the surface is often unknown, especially under oxidizing conditions. The redox properties of the catalyst are typically investigated by temperature programmed reduction and oxidation or x-ray absorption spectroscopy. However, these are not the surface sensitive techniques and provide limited surface details especially under H_2/H_2O environments. We report the use of in-situ x-ray photoelectron spectroscopy (XPS) to determine the oxidation state of Co following exposure to O_2, H_2, and H_2/H_2O. We found that the type of support and catalyst pretreatment (calcinations and/or reduction temperature) have a strong effect on the Co^0/Co^{2+} ratio. Our results indicate that Zn helps stabilize Co against oxidation by O_2 or H_2O. The in-situ XPS measurements allowed us to study the effect of Co^0/Co^{2+} ratio on the catalytic activity and understand the role of Co^{2+} in the ethanol reforming reaction pathways. The catalytic tests show that both Co^0 and Co^{2+} were active in the C-C bond cleavage and water gas shift reactions. However, Co^0 is shown to be much more active than Co^{2+}. Also, the reaction pathways for CO_2 and CH_4 formation appear to be different on Co^0 and Co^{2+}. Catalysts with higher Co^0/Co^{2+} surface ratio exhibited lower selectivity to CH_4. Our results show that ethanol decomposition and CO methanation are more favored on Co^{2+} relative to Co^0. In addition, we show that on both Co^0 and Co^{2+}, CO_2 is a secondary product forming by the water gas shift reaction.

AS-TuP22   Surface Characterization of Al-Si-Fe-X (X = none, Sb, V) Rapidly Solidified Ribbons, *V.N. Gaidarova*, Bulgarian Academy of Sciences, Bulgaria, *Y.T. Yordanov*, Sofia Technical University, Bulgaria

Al-Si alloys are used in the automotive industry. Improvement of their properties is achieved by rapid solidification (RS) [1]. Highly developed surface of RS material is of importance in both interaction with the environment and processing of materials during ingots production. Surface formation and development under thermal treatment depends on the alloying and modifying elements.

Al-Si under-eutectic alloys with addition of Fe, Sb, V in different combinations are produced by RS using Planar Flow Casting technique. As-cast and thermally treated samples are studied using Auger Electron Spectroscopy (AES) combined with argon ion sputtering.

AES depth profiles of as-cast specimens demonstrate formation of nanoscale aluminum based oxide, enriched layer (EL) with solute elements and a region of constant Al/Si content following in depth. Annealing up to moderate temperatures (≤ 638K) causes changes in thickness of both oxide scale and EL. Availability of Fe (≤ 2wt.%) promotes diffusion of solute elements in oxide and EL while addition of Sb, even in a minor quantity 0,17 wt.%, to the last alloy content decreases Si-segregation. Changes are not detected in the oxide or EL of (Fe+V) doped RS ribbons. Annealing up

to temperatures ≥ 673K leads to ceasing of oxidation and diminishing of silicon enrichment for all studied Fe-containing RS alloys. These remarkable changes of elements distribution can be connected with crystallization of Fe-containing phase at oxide/bulk interface and growth of silicon precipitations. Registered solute enrichment is in agreement with the segregation prediction [2], which is based on the phase diagrams of alloys. Comparison with micro hardness measurements on the surface of the ribbon samples shows proportional dependence on the uniform distribution of the fine silicon precipitations. With their growth the micro hardness declines, excluding for the RS alloy doped with Fe+V. In the last case dopands content does not allow iron segregation at the surface, which evidently leads to hardening by finely dispersed Fe-containing particles in the Al-matrix under.

References:

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AS-TuP23   Characterization of a Self-assembled Molecular Nanolayer at Buried Cu-silica Interface, *S. Garg, R. Teki, A. Jain, K. Chinnathambi, B. Singh,* Rensselaer Polytechnic Institute, *V. Smentkowski,* GE Global Research Center, *M. Lane,* Emory and Henry College, *G. Ramanath*, Rensselaer Polytechnic Institute

Integration of metal-dielectric interfaces using molecular nanolayers (MNLs) is attractive for prospective applications such as laminates in high frequency electronics and packaging, nanodevice wiring and composites. Recent works have shown that annealing-induced siloxane bridging can toughen organosilane-functionalized copper-silica interfaces. While strong bonding of the MNL with the under- and over-layers is essential for promoting adhesion, the nature of the MNL structure and bonding, especially at temperatures where the MNLs are known to degrade on bare surfaces, are unclear. But tracking atomic-level intermixing and interfacial phase formation in a sub-nm-layer is an exacting challenge due to difficulties in distinguishing Si atoms in the organosilane MNL from Si atoms in the silica substrate, and obtaining sufficient contrast by electron microscopy. Here, we study organogermane-tailored interfaces using a combination of electron spectroscopy and microscopy, and density functional theory calculations to obtain insights into the interface chemical changes. Our results reveal that annealing decomposes the organic monolayer into an inorganic Cu-O-Si network, leading to interface toughening.

We assembled Benzyl-trichlorogermane (BTCG) on silica to form a 0.7-nm-thick nanolayer. Four-point bending fracture tests on as-prepared Cu/BTCG/SiO$_2$ sandwiches revealed a low interface toughness of 2.1 J/m^2, comparable to pristine Cu/SiO$_2$ structures. However, interfacial toughness increased monotonically with annealing temperature, yielding values as high as 23.3 J/m^2 for T$_{anneal}$ = 500 ºC. Core-level spectra from silica fracture surfaces show a strong Ge signature for T$_{anneal}$ $\leq$ 300 ºC that becomes undetectable for T$_{anneal}$ $\geq$ 400 ºC, suggesting Ge transport and destruction of the organic MNL. This result is corroborated by time-of-flight secondary ion mass spectroscopy (SIMS) profiles showing the smearing of the interfacial Ge spike into the silica layer upon annealing. Incorporation of Ge in the silica weakens the Si-O-Si network, leading to intermixing of Si, O and Cu, forming nanoscale islands of rhombohedral CuSiO$_3$ observable by cross-sectional transmission electron microscopy and X-ray spectroscopy. For pristine Cu/SiO$_2$ structures there were no changes at the interface and the toughness value was $\sim$ 3 J/m^2 for T$_{anneal}$ $\leq$ 700 °C. Our findings suggest that molecular degradation of the organic MNL to form nanoscopic layer of inorganic metal-oxide-silicon bonds could be an attractive approach for toughening interfaces.

AS-TuP24   Experiences with the High Energy Resolution Optics (HERO) Update on a Physical Electronics 690 Auger System, *W. Wallace, J.A. Ohlhausen, M.T. Brumbach*, Sandia National Laboratories

We will present our experiences with the new High Energy Resolution Optics (HERO) upgrade on a Physical Electronics Auger 690 system. This upgrade allows the single pass cylindrical analyzer in the Auger system to achieve higher energy resolution than in the standard mode. With this upgrade, it should be possible to separate chemical states for certain elements. Also, it should be possible to separate closely spaced peaks from selected elements that have been difficult or impossible to separate without the upgrade. Specifically, we will investigate practical use of this upgrade in the analysis of materials systems where overlapping peaks have historically been an issue, such as Kovar, which consists of the elements Ni, Fe and Co. Strategies for the successful use of the technique as well as its current limitations will be shown.

AS-TuP25 A Device for Traceable Force Probe Calibration, *J.F. Portoles, P.J. Cumpson*, Newcastle University, UK

AFM has become in the last two decades an instrument for the measurement of forces in the piconewton range, including forces at the single molecule level. Although many methods have been developed for the force calibration of AFM cantilevers [1], these use to be affected by high uncertainties and sometimes difficulty of use. Furthermore there is a growing need for a traceable force calibration standard that provides traceability to the units of the SI [2] and therefore allows comparison between instruments and with related force measurement techniques such as the Optical Tweezers and the Biomembrane Force Probe. We present the development of a device that provides fast and easy force calibration of AFM cantilevers and other force probes, simultaneously facilitating the dissemination of force and providing traceability to the units of the SI.

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AS-TuP26 Synthesis and Characterization of System Sr(Ru$_{1-x}$Fe$_x$)O$_3$ type Perovskite, *L. Huerta, J.L. Mazariego, M. Quintana,* Universidad Nacional Autónoma de México, *E. Ramírez,* Universidad Autónoma de la Ciudad de México, *M. Flores,* Universidad de Guadalajara, México, *R. Escamilla*, Universidad Nacional Autónoma de México

Polycrystalline samples of the SrRu$_{1-x}$Fe$_x$O$_3$ system with x = 0, 0.25, 0.5, 0.75 and 1.0, were synthesized by solid state reaction of stoichiometric quantities of oxides of RuO$_2$, Fe$_2$O$_3$ and SrCO$_3$. The samples were characterized by X-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS) and ac magnetization vs. temperature measurements. XRD results shown that the lattice parameter decreases with the iron content; as a consequence the unit cell volume decreases. The Sr 3d, Ru 3d Fe 3d and O 1s spectral lines associated to the chemical states of Sr(Ru$_{1-x}$Fex)O$_3$ were identified by XPS. Curves of ac magnetization vs. temperature shown for x $\geq$ 0.25 a behavior spin glass.

AS-TuP27 Surface Energy, Topography & Composition of SiOx on Polycarbonate by Proton-Induced X-ray Emission (PIXE), Atomic Force Microscopy & Sessile Drop Contact Angle Analysis using Young-Dupre Equation., *Q.B. Xing,* Arizona State University, *C.F. Watson,* SiO2 Associates, LLC, *M.A. Hart, D.A. Sell, J.D. Bradley,* **R.J. Culbertson**, *A.S. Benitez-Brady,* Arizona State University, *B.J. Wilkens,* LeRoy Eyring Center for Solid State Science at Arizona State University, *N. Herbots*, Arizona State University

The surface energy of silica is correlated with topography and composition in micron thick films on polycarbonate visors for football, hockey, ski and scuba diving.

Use of visors can be limited by condensation that occurs in during athletic performance. Control of the hydro-affinity of the surface requires an understanding of hydrophobic/hydrophilic behavior as well as of condensation kinetics and surface contamination for up to several continuous hours

Combining Proton-Induced X-ray Emission (PIXE), Tapping Mode Atomic Force Microscopy (TMAFM) & the Sessile Drop Method with Contact Angle Analysis (CAA) using Young-Dupre Equation, yields insights into nucleation and ripening of water droplets. Real-time observation via optical microscopy of both reflected and transmitted light, PIXE, TMAFM and CAA with previous Rutherford Backscattering Spectrometry (RBS) results ca establish a model to predict surface energy and hydro-affinity of silicates, phospho-silicates and other compounds used for high impact resistance vision wear coatings. Ultimately, the goal is to control condensation on such coated polymers for applications in sport eyewear used in hockey, skiing, football and other contact sports, swimming goggles, and diving masks.

Surface characterization techniques in this research combine the 4.265 ± 0.035 MeV 12C(alpha, alpha)12C and the 3.05 ± 0.005 MeV 16O(alpha, alpha)16O MeV Oxygen Nuclear Resonance to increase light atoms detection with 2.8 MeV Hydrogen Elastic Recoil Detection for compositional analysis with depth profiling, and Tapping Mode Atomic Force Microscopy for surface topography. The water affinity of the solid surface is measured via contact angle analysis using the Sessile Drop method calibrated with standards such as OH(1x1)Si(100), 100 nm thermal oxides on Si(100), Si(100) amorphized by high dose Si ion implantation at 35-175 keV, alpha-quartz crystals, and the Young-Dupré equation to compute surface energy. The surface energy is then correlated with statistical analysis of Tapping Mode Atomic Force Microscopy topographs and PIXE/RBS analysis to predict and determine the mechanism and kinetics of water condensation. Polymer adsorption on these surfaces is used to alter the surface hydroaffinity and maintain clarity when condensation occurs by making it hydrophilic [1].

[1] US Patent pending "Molecular films for controlling hydrophobic, hydrophilic, optical, condensation and geometric properties of Si-based surfaces. Inventor(s): N. Herbots, J. D. Bradley, M. A. Hart, D. A. Sell, S. D. Whaley, Q. Bradley (filed: November 9, 2009)

AS-TuP28 An Investigation of Primary Ion Choices in Depth Profiling Using Time-of-Flight Secondary Ion Mass Spectrometry, *Z.H. Zhu*, *V. Shutthanandan*, Pacific Northwest National Laboratory

Depth profiling is one of the important applications of time-of-flight secondary ion mass spectrometry (ToF-SIMS). Dual beam depth profiling strategy is commonly used because the current of the primary ion beam is normally very weak (~10^{-12} A), and the second beam with high current (10^{-8}-10^{-6} A) is introduced for sputtering. Recent years, a major development in ToF-SIMS field is application of cluster primary ions. It has been found that cluster primary ions can dramatically enhance signal intensity of molecular ions with a factor of 10-1000. So far, cluster primary ions have been introduced into commercial ToF-SIMS instruments for over five years. However, in presently available commercial ToF-SIMS instruments, the usable currents of cluster primary ion beams are considerably smaller than that of monatomic primary ion beams. More importantly, enhancements using cluster primary ions are not only material-dependent but also ion species-dependent. Therefore, large amounts of experimental data are needed to develop an understanding of how to choose an optimal primary ion for ToF-SIMS depth profiling.

In this work, we studied depth profiling of several representative systems: (1) Hydrogen depth profiling in silicon wafer, zinc oxide crystal and normal glass; (2) molecular depth profiling of a thin sucrose film on silicon substrate; (3) molecular depth profiling of Irganox "delta" layers prepared by NPL, United Kingdom . Six primary ion beams (25 keV Bi$^+$, Bi$_3^+$, Bi$_5^+$, 50 keV Bi$_3^{++}$, 10 keV C$_{60}^+$ and 20 keV C$_{60}^{++}$) were compared. Our data show that enhancement of cluster primary ions for elemental species is limited (~1.5-4.0 times) if compared to that for molecular species (>>10 times). Considering the highest usable currents of difference primary ion species on presently available commercial ToF-SIMS instruments, we suggest that monatomic primary ion beams may be the best choice for elemental depth profiling, and cluster primary ion beams are better choices for molecular depth profiling.

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