

Tuesday Afternoon Poster Sessions

Applied Surface Science Division

Room: East Exhibit Hall - Session AS-TuP

Applied Surface Science Poster Session

AS-TuP2 An Electrostatic Analytical Microscope for SEM/SAM Surface Studies with 3nm-7nm Spatial Resolution, A.R. Walker, M. Rignall, Shimadzu Research Laboratory (Europe) Ltd., UK

A very high spatial resolution all electrostatic, ultra high vacuum, electron optical column has been developed for fast Nano analysis of specimen surfaces. The electron optical column does not project any electric or magnetic fields to the analysis region or beyond.

The electrostatic column operates with a beam energy range of 1-10keV, at a specified working distance of 10mm, for all survey and analytical modes of operation. Spatial resolutions of 4-7nm for Auger Nano analysis and 3nm for a SEM mode correspond to probe currents that range from 1nA to 0.25nA. Other modes of operation are available and these include operation at intermediate spatial resolutions <100nm with high probe currents of 100's nA and a very useful wide survey mode of ~5mm field of view at lower spatial resolutions <1 μ m. The electron optical column, having no magnetic lens components and therefore no hysteresis effects, is able to switch fast between these different modes.

Key to the electron optical column specification is the design of the probe forming electrostatic objective lens which operates in an accelerating mode. This lens design is a compact truncated cone with 80° apex angle at the analysis position (10mm WD) which enables a wide angular access (50°) to the specimen surface. Its electron optical design is an Einzel lens of asymmetrical electrode structure and operates with a positive potential of up to 50kV applied to its central electrode. The lens operation is extremely stable with no detectable electrical instabilities.

To aid the development of the electrostatic lens we use simulation software to calculate the lens parameters. At the objective lens WD of 10mm and object at infinity, low values of spherical aberration (75mm) and chromatic aberration (19mm) were computed. These values are comparable to the best magnetic lenses of similar external dimensions and working distance.

The column is mounted on a small analytical chamber for test purposes. We have demonstrated a 3nm SEM spatial resolution at beam energies of 10keV with 250pA of current. At a beam energy of 3keV with 150pA of current, we achieved and 7nm SEM spatial resolution.

An Auger signal was detected using a new form of hyperbolic field parallel energy analyser. A Gold Au (64eV) line scan demonstrated an edge resolution of 4.1nm using a primary probe of 10keV energy and 400pA of current.

For conventional energy analyzers, a probe current of 1nA is more appropriate and the spatial resolutions have been measured as 5nm and 7nm for respective beam energies of 10keV and 7keV.

AS-TuP3 Core Level Shift from Experiment and First-Principles-Theory – A Comparison, B. Kiefer, New Mexico State University, B. Halevi, K. Artyushkova, University of New Mexico

The knowledge of geometries and chemistry of functional motifs that causes particular materials behavior is crucial for the rational development of novel materials and materials based technologies. X-ray photoelectron spectroscopy (XPS) measures the binding energy (BE) changes that are induced on an atom by its surrounding ligands and by comparing to them to databases. However, in many cases the reference materials available in the databases are limited to common/model compounds, while actual materials designed may have more complicated chemistries. Furthermore, the big spread in the reported values of BE due to various ways to charge calibrate spectra and also sensitivity of BE to secondary environments present a big problem for accurate identification of unknown peaks in spectra.

Being able to calculate binding energy shifts based on molecular structure can be very important tool for identifying structural motifs in materials. There are only a few studies reporting density-functional-theory (DFT) calculations of BE energies due to challenges that are associated with the treatment of core electrons. Their high kinetic energy can require to include relativistic effects especially for heavy elements and absolute values of binding energies cannot be expected to be accurate. Furthermore the differences in reference state complicate the direct comparison between experiment and theory.

A possible solution to these challenges is to compare BE to a reference system that is accessible both in experiment and theory. We will report on BE shift that have been calculated and compared to experimentally obtained values for metallic, bimetallic and covalent systems. For metallic Pd (111) system, surface layers have lower binding energy, while sub-surface is bulk like. For bimetallic PdZn system, Pd(3d) and Zn(2p) shift upward with respect to fcc-Pd(3d) and for hcp-Zn(2p), respectively. Magnitudes of shifts are very similar to that obtained experimentally. For covalent system, such as metal-less and metal-containing porphyrins, shift for N 1s BE in Co 2p environment compared to N 1s without metal is also very close to that obtained experimentally.

AS-TuP4 Evaluation of C₆₀ Depth Profiling Conditions for XPS Organic Films Analysis, S. Alnabulsi, S.R. Bryan, J. Moulder, Physical Electronics

Type-II organic materials can be successfully depth profiled by XPS using C₆₀ ion beam sputtering at room temperature. Success is defined by achieving steady state composition as a function of depth. However, depth profiling of Type-I polymers have been marginally successful due to rapid sample damage under C₆₀ bombardment. The use of high C₆₀ beam energy at a glancing angle has been shown to extend the maximum depth of successful depth profiling, yet it eventually fails due to sample roughening, concomitant carbon build up, and a strong reduction in sputter rate.

Zalar (azimuthal) rotation has been shown to minimize sputter induced roughness formation, improve depth resolution in multi-layer film structures, and allow depth profiles to be extended to even greater depths. Cooling of the sample to below its glass transition temperature is expected to reduce the mobility and reactivity of free radicals that are formed during the sputtering process.

The purpose of this study is to evaluate the relative importance of using Zalar rotation and sample cooling to characterize standard organic thin film structures and to quantify the benefit to using them simultaneously.

AS-TuP5 Development and Application of Novel Electron Energy Analyzers for Chemical Analysis of Surfaces, D. Cubric, Shimadzu Research Laboratory (Europe) Ltd., UK, N. Kholine, Institute for Analytical Instrumentation, RAS, Russian Federation

Various instruments have been developed previously for analyzing the spectrum of energies of beams of charged particles emanating from surfaces and described in numerous publications [1]. Among all those instruments the concentric hemispherical analyser (CHA) and the cylindrical mirror analysers (CMA) have been the most often used instruments both commercially and for various devices developed by different laboratories. At first sight, geometry of the two analyser types is very different. However, topologically their geometries are very similar. This paper presents a line of thought where geometries of both analysers are just particular examples of a more general geometry that in turn provides numerous analyser configurations, that we now call spheroid energy analysers (SEA), often having excellent electron optical characteristics [2]. The SEA instrumental concept enables electron optical exploration of various new analyser embodiments, particularly well suited for chemical analysis of surfaces and surface nano-features. Progress in this instrumentation development and example spectra will be presented. **References** [1] D. Roy and D. Tremblay, Design of electron spectrometers, Rep. Prog. Phys. 53 (1990) 1621-1674 [2] D. Cubric, N. Kholine and I. Konishi, doi:10.1016/j.nima.2010.12.146

AS-TuP6 Extreme Brightness: Reaching the Ultimate Limits of the Electron Beam, J.D. Jarvis, J.L. Kohler, B. Ivanov, N. De Jonge, B.K. Choi, A.B. Hmelo, C.A. Brau, Vanderbilt University

We report recent results from field emission microscopy studies of multiwall carbon nanotubes (MWCNT) and from energy spectrum measurements of beams from diamond field emitters (DFE). As expected, resonant tunneling through adsorbed species on the emitter surface is an important and sometimes dominant effect. For diamond emitters our observations include order-of-magnitude emission enhancement without spectral broadening, complex spectral structure, and sensitivity of that structure to the applied electric field. For carbon nanotubes we have observed electron beams from individual adsorbates which are estimated to approach the maximum beam brightness allowed by Pauli exclusion.

The development of CNTs as field emitters for the purposes of microscopy, lithography, radiation generation, and display production has been a protracted endeavor. Working in their favor, CNTs have excellent emission stability, high activation energy for thermal migration, excellent current throughput capacity, and a high degree of chemical inertness. Not

surprisingly, these properties extend to other covalent-carbon structures such as CVD diamond field emitters. DFEs have shown great promise as high-brightness electron-beam sources in recent years. One of the more exciting revelations regarding CNTs and DFEs has been the realization that resonant tunneling through adsorbed species can be exploited for the generation of multi-microamp-level beams with perfect transverse coherence.

For resonant tunneling through a single molecule the electron source size is on the order of the electron wavelength. Estimates of the transverse momentum spread of the resulting electron beams suggest that the transverse emittance is Heisenberg limited. Such beams have been produced using single atom tungsten, or single atom noble-metal field emitters, however the relatively weak binding of the metal atoms has limited the total current that can be extracted to the sub-microamp regime. In this paper we will discuss our efforts to generate, stabilize, and characterize, multi-microamp beams from individual molecules on CNTs

AS-TuP8 Surface Characterization of Disposable Laboratory Gloves by X-ray Photoelectron Spectroscopy (XPS). *B.R. Strohmeier, C. Baily, T.S. Nunney*, Thermo Fisher Scientific, UK, *A. Plasencia*, Thermo Fisher Scientific, *J.D. Piasecki*, RJ Lee Group, Inc.

Disposable elastic gloves are ubiquitous in scientific laboratories and are also widely used in many industries during handling of critical surfaces. Disposable gloves are typically made from nitrile, latex, neoprene, or other polymers and offer their users protection from various aqueous acids and bases, biological fluids, organic solvents, and other potentially harmful chemicals. A second major application of disposable gloves is to protect manufactured products and analytical samples from contamination caused by the transfer of skin cells, oils, salts, or other residues resulting from contact with bare hands. However, disposable gloves can also be a potential source of contamination. In addition to the primary polymer structure, many types of common laboratory gloves also contain a variety of inorganic materials in the glove formulation. Mold-release agents that allow the gloves to be easily stripped from the glove formers during fabrication may be present on glove surfaces. Furthermore, many types of disposable gloves have polymeric surface coatings that provide improved donning properties. Contamination resulting from surface residues on gloves can adversely affect materials used in industries where surface cleanliness is essential for optimum product performance and can also interfere with the analysis of samples depending on the specificity and sensitivity of the analytical technique. X-ray photoelectron spectroscopy (XPS) is a qualitative and quantitative surface sensitive technique that can be used to evaluate the surface composition of disposable gloves and to determine if contamination transfer occurs from gloves in a specific process. In this study, XPS was used to characterize the surface compositions of a variety of common laboratory gloves. The transfer of surface components from gloves to other material surfaces and changes in the surface composition of gloves following exposure to several common laboratory solvents were also investigated.

AS-TuP10 Large Area Cross Sectional Microstructural Characterization of ToF-SIMS Depth Profile Crater Walls. *V.S. Smentkowski, D. Ellis*, GE-GR

Focused Ion Beam (FIB) techniques are widely used in order to generate cross sections of samples which can then be analyzed using a variety of analytical instrumentation in order to obtain microstructural information. In order to rapidly generate FIB cross sections, small areas (typically 5 to 10 microns) are milled. Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is a powerful surface analytical technique that is able to measure low concentrations of sub surface species. ToF-SIMS depth profile measurements are collected by eroding a large area (50 to 1,000 microns in size) of a sample using an ion beam for a certain amount of time, pausing the erosion, analyzing a smaller (central) region of the eroded area, and repeating the cycle until the desired depth has been reached. Ion images are often recorded at each depth and a full mass spectrum is saved at every volume element allowing for 3 D analysis. Often times, both ToF-SIMS depth profile analysis and high resolution microstructural SEM characterization are required on the same sample. Ideally, these complimentary analyses would be performed in the same region of a sample. In this presentation, we will demonstrate that FIB techniques can be used to clean up the large area craters produced by ToF-SIMS depth profile analysis thereby enabling microstructural characterization over larger areas of samples.

Advantages of this approach are: larger FIB cross sections can be prepared since a significant amount of material was removed during the erosion cycles in the ToF-SIMS analysis, combining the chemical information provided from the ToF-SIMS analysis with the large area microstructural characterization provided by FIB-SEM analysis, and having both the ToF-SIMS and the large area cross sectional analysis performed in the same region of the sample. The ToF-SIMS depth profile craters have a slope of

about 45 deg (the ion column is positioned at an angle of 45 deg from the sample normal), and hence an advantage of performing the FIB clean up at this angle is the enhancement in the layer thickness that will be available for microstructural analysis.

AS-TuP11 Microphase Separation of Various Diblock Copolymers Investigated by TOF-SIMS Depth Profiling. *Y. Lee*, Korea Institute of Science and Technology, Republic of Korea, *J. Lee*, Korea University, *W.C. Lim*, Korea Institute of Science and Technology, *K. Shin*, Sogang University, Korea, *K.-J. Kim*, Korea University

Diblock copolymers, composed of two distinct homopolymers covalently bonded together at one end, exhibit a microphase separation from a disordered state to an ordered state on cooling or heating. The microphase separation of diblock copolymers has been investigated by many different research groups for many years, because of the increasing use of diblock copolymers as compatibilizers, dispersants, impact modifiers, nanocarriers, and templates. Investigation of the phase behaviour of a family of diblock copolymers between styrene and a homologous series of methacrylates or acrylates has revealed that significantly different phase behaviours are seen for these materials, depending on the temperature, molecular weight, and alkyl side chain length. In this work, we characterized the morphology from various diblock copolymers of poly(styrene-*b*-alkyl acrylate)(PS-PAA), where PS block was perdeuterated, near the copolymer/air and copolymer/substrate interfaces and in the bulk using time-of-flight Secondary Ion Mass Spectrometry (ToF-SIMS). ToF-SIMS Depth Profiling was obtained for the lamellar morphology of PdS-PAA which is found to orient parallel to the surface of the substrate. This preferential orientation resulted in a periodic variation in the composition of each block that continued through the entire copolymer film. Temperature- and chain length-dependent annealing studies on PdS-PAA thin films on the silicon substrates were performed to investigate the order-to-disorder transition (ODT) properties of diblock copolymers.

AS-TuP12 Analysis of Passivated Surfaces for Mass Spectrometer Inlet Systems by Auger Electron and X-Ray Photoelectron Spectroscopy. *H.M. Ajo, D.W. Blankenship, E.A. Clark*, Savannah River National Laboratory

Stainless steel coupons approximately 0.5" in diameter and 0.125" thick were passivated with five different surface treatments and an untreated coupon was left as a control. These surface treatments are being explored for use in tritium storage containers. These coupons were made to allow surface analysis of the surface treatments using well-known surface analysis techniques. Depth profiles using Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) were performed on these coupons to characterize the surface and near surface regions. Scanning electron microscope (SEM) images were collected as well. All of the surface treatments studied here appear to change the surface morphology dramatically, as evidenced by lack of tool marks on the treated samples. In terms of the passivation treatment, Vendors A-D appeared to have oxide layers that were very similar in thickness to each other (0.7-0.9 nm thick) as well as the untreated samples (the untreated sample oxide layers appeared to be somewhat larger). Vendor E's silicon coating appears to be on the order of 200 nm thick.

AS-TuP13 Surface Characterization of Gunshot Residue (GSR) by X-ray Photoelectron Spectroscopy (XPS) and High Resolution Electron Microscopy. *A.J. Schwobbe*, RJ Lee Group, Inc., *B.R. Strohmeier*, Thermo Fisher Scientific, *K.L. Bunker, D.R. McAllister, J.P. Marquis, Jr., J.D. Piasecki, N.M. McAllister*, RJ Lee Group, Inc., *W. Sgammato*, Thermo Fisher Scientific

Discharged firearm cartridges produce unique microscopic particles referred to as gunshot residue (GSR). GSR is primarily composed of the products of combustion of the cartridge primer materials and typically contains varying amounts of Pb, Sb, and Ba, plus other elements. GSR particles can range in size from tens of nanometers to hundreds of micrometers. Because of the high temperatures (~1,500-3,600 °C) and pressures (~14,000-65,000 psi) that result within 1 millisecond of discharging a firearm cartridge, highly complicated chemical interactions are likely to occur that will affect the chemical composition of the GSR particles. Computer-controlled scanning electron microscopy (CCSEM) is the method preferred by the forensic community for the automated analysis of GSR. With CCSEM, large populations of potential GSR particles in the size range of ~1-10 µm are rapidly screened for the characteristic presence of combinations of Pb, Sb, and Ba using energy dispersive X-ray spectroscopy (EDS). Determining the presence of these three elements fused together in a single particle having the correct morphology is all that is normally required for the positive identification of GSR. CCSEM, however, does generally not provide information regarding the population of particles much less than 1 µm. In addition, little is presently known regarding the surface chemistry of GSR. Because of its nanometer-scale sampling depth and the ability to provide

detailed chemical state information, X-ray photoelectron spectroscopy (XPS) can provide important information regarding the surface chemistry of GSR. This work examines the fine fraction of GSR particles with high resolution electron microscopy methods and complements the microscopy data with surface chemistry information obtained from XPS.

AS-TuP14 Analysis of Graphene and Other Graphitic Materials using XPS and AES, H.M. Meyer III, Oak Ridge National Laboratory

Synthesis and characterization of advanced carbon materials, including graphene, has accelerated over the past several years at the Oak Ridge National Laboratory. Projects include, among others, the development of nanostructured carbon materials for batteries, fuel cells and as supports for revolutionary catalysts. The past year has also brought to ORNL new projects related to the growth, characterization and application of graphene. This poster will highlight x-ray photoelectron spectroscopy and scanning Auger microanalysis of a variety of important carbon materials from several of these research projects, including nano-sized carbon powders for battery applications, graphitic carbon powders used in fuel cells, graphene flakes synthesized for supporting catalyst materials and CVD grown graphene. In particular, an approach for curve fitting highly graphitic materials will demonstrate internally consistent results, giving insight into the sp^2 vs. sp^3 type carbon atoms present in the material.

Research sponsored by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of FreedomCAR and Vehicle Technologies, as part of the High Temperature Materials Laboratory User Program, Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract number DE-AC05-00OR22725.

AS-TuP15 Investigation of Precious-Metal/Metal-Oxide-Support Interactions in Automotive Catalytic Converters using a Pd/Ce_{0.7}Zr_{0.3}O₂ Model Planar Catalyst System, O.K. Ezekoye, University of Michigan, M.I. Nandasiri, Western Michigan University, T. Varga, P. Nachimuthu, W. Jiang, S.V.N.T. Kuchibhatla, S. Thevuthasan, Pacific Northwest National Laboratory, X. Pan, G.W. Graham, University of Michigan

Ceria-zirconia mixed oxide (CZO) has been incorporated into automotive catalysts as a support material for precious metals (Pt, Rh, Pd) due to its highly desirable redox properties. However, at high operating temperatures, certain interactions between CZO and precious metal particles may adversely affect the performance of the catalytic converter. Thus, it is important to investigate the CZO/precious-metal interactions under redox conditions. Here, the preparation of Pd/CZO thin films as model planar catalyst systems will be described together with a systematic study of an important adverse interaction, the encapsulation of Pd particles by CZO, using a combination of x-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM).

Ceria-zirconia ($Ce_{0.7}Zr_{0.3}O_2$) thin films with thickness ranging from 10-200 nm were grown on (111) yttria-stabilized zirconia (YSZ) by oxygen plasma assisted molecular beam epitaxy (OPA-MBE). The epitaxial layer growth of CZO on YSZ(111) was confirmed by in-situ reflection high energy electron diffraction (RHEED). Atomic force microscopy (AFM) images revealed the smooth surface of the films with low roughness values (3-8 Å). Rutherford backscattering spectrometry (RBS) data along channeling and random geometries showed the minimum yield (χ_{min}) of 13% for Ce with no inter-diffusion of metal atoms at the film/substrate interface. The single crystal nature of the film with CZO(111) orientation was confirmed by XRD data. Following the growth and characterization of thin films, ~1 monolayer of Pd was deposited on CZO(111) by thermal evaporation in a UHV chamber. After air calcination at 600 °C, the Pd/CZO films were reduced in 1% H_2/N_2 at 200°C, followed by annealing in N_2 at 700 °C. Due to the additional reduction-induced compressive stress, the 10 nm and 40 nm films broke up and formed a rough surface with 10-20 nm CZO mesas, as observed by HRTEM. However, films with a thickness above ~50 nm were stable, and Pd particles that formed on the surface became partially encapsulated by migration of CZO. In the films with a thickness above ~50 nm, the native compressive stress induced by the lattice mismatch between the film and substrate was relaxed by misfit dislocations at the interface, as revealed by high resolution scanning TEM images, to varying degree, depending on film thickness, but the extent of encapsulation appeared to be about the same for all film thicknesses. These results suggest that the driving force for the partial encapsulation resides in the nature of CZO, and is not simply a consequence of the lattice-mismatch-induced compressive stress in the films.

AS-TuP17 Cleaning and Characterization of InP Surface using Atomic Hydrogen and STM, W. Melitz, J. Shen, T. Kent, University of California San Diego, R. Droopad, Texas State University, P.K. Hurley, Tyndall National Institute, A.C. Kummel, University of California San Diego

Metal oxide semiconductor field effect transistors (MOSFETs) are the dominant logic device in modern electronics. Due to the challenges of scaling Si-MOSFETs alternative materials are being explored to improve device performance. III-V semiconductors are of interest for use in MOSFETs due to their high mobilities, but in order to make these devices competitive the semiconductor-oxide interface needs to have a low density of interfacial traps (D_{it}) in order to minimize subthreshold swings and also be atomically flat to allow high mobility at high field strengths. Current Si-MOSFET fabrication uses a gate last process which is an attractive method because it minimizes the gate oxides exposure to harsh processing conditions. In order for gate last processing to provide a nearly defect free semiconductor-oxide interface for surface channel devices, the channel surface must be in pristine condition before the oxide layer is deposited. In addition the oxide deposition process cannot introduce any defects. Recent advances show that a thin indium phosphide layer deposited on top of the InGaAs channel may provide superior electronic performance because the InGaAs/InP interface is defect-free and flat while the defects at the oxide/InP interface are less detrimental to device performance than the defects at the oxide/InGaAs interface.

In order to facilitate gate last processing of the InP/InGaAs channel stack, a four step process was investigated to clean and nucleate atomic layer deposition (ALD) of an InP/InGaAs surface. Samples were grown with an undoped 2 nm InP layer on ~1 μm InGaAs layer doped with $4 \times 10^{18} cm^{-3}$ of Si on an InP wafer. Using in-situ atomic imaging (scanning tunneling microscopy), electronic measurements (scanning tunneling spectroscopy), and XPS a four step in-situ process was developed for converting an air-exposed InGaAs(100)-4x2 surface into a flat, electronically passivated, mono-layer nucleation template for ALD of gate oxides. The optimized process includes a small dose of atomic hydrogen, annealing to reduce surface roughness, TMA dosing to functionalize the surface, and a final annealing to induce a highly ordered ALD nucleation layer. Following atomic hydrogen cleaning at 380°C and annealing at 470°C, the surface was exposed to $\sim 1 \times 10^{-2}$ Torr of TMA at room temperature and annealed to 270°C. The TMA induces a surface reconstruction consistent with a bulk like bonding configuration between the Al atoms and the surface P atoms. The TMA passivation layer has horizontal rows of DMA. The cleaning and nucleation process does not disrupt the InP surface thereby providing a path for further scaling of the InP layer and the gate oxide.

AS-TuP18 Highly Selective and Low Damage Etching of GaAs/AlGaAs Heterostructure using Cl₂/O₂ Neutral Beam, J.S. Oh, K.S. Min, C.K. Kim, G.Y. Yeom, Sungkyunkwan University, Korea

Highly selective and low damage etching of the GaAs cap layer on AlGaAs is essential in fabricating devices such as heterojunction superlattices, field effect transistors, injection lasers, and solar cells, etc. The GaAs on AlGaAs was etched using a low energy Cl_2/O_2 neutral beam and the schottky device characteristics fabricated on the exposed AlGaAs were compared with those fabricated after the etching using wet etching and a Cl_2/O_2 ion beam. The wet etching was conducted by a mixture of H_2O_2 and H_3PO_4 . For the Cl_2/O_2 neutral beam etching, a neutral beam system composed of three-grid inductively coupled plasma (ICP)-type ion gun and a reflector installed just in front of the ion gun was used. Using a low energy Cl_2/O_2 ion beam or a Cl_2/O_2 neutral beam, highly selective etching of the GaAs cap layer to AlGaAs similar to wet etching could be achieved through the formation of Al_2O_3 on the exposed AlGaAs during the etching. When the electrical characteristics of the schottky devices were compared, the devices fabricated after the etching using the neutral beam showed the best electrical characteristics such as electrical stability, low leakage current, higher barrier height, etc. by showing low damage to the exposed AlGaAs surface.

AS-TuP19 TiO₂ Nanotube Growth Mechanism Studied with Scanning Auger Spectroscopy, D.F. Paul, Physical Electronics, S. Berger, F. Schmidt-Stein, S.P. Albu, H. Hildebrand, P. Schmuki, University of Erlangen-Nürnberg, Germany, J.S. Hammond, Physical Electronics

Anodic TiO_2 nanotubes offer unique properties for a wide range of applications including energy conversion, photocatalysis and biomedical devices^{1,2,3}. It is widely accepted that the initial growth of the nanotubes is based on the formation of a compact anodic oxide followed by the formation of etching grooves and pores in the oxide^{4,5}. The mechanism of steady state growth of the nanotubes from the embryonic pores has, however, remained a topic of debate. To evaluate a flow model^{1,6} for the formation of the tubular structures, high spatial resolution Scanning Auger Spectroscopy data is used to elucidate the compositional variations across TiO_2 nanotube layers grown in a fluoride containing ethylene glycol electrolyte. The layers were fractured parallel to the axes of the nanotubes

and quantitative spectra, line scans and elemental maps were acquired along the walls of the nanotubes. The Auger data indicates the presence of a fluoride rich layer located between the tube walls, and in particular, the triple points of the hexagonally ordered nanotube arrays. This data supports fluoride dissolution as the reason for a transition from a porous oxide layer to tubular structures. This data also supports a flow model as a mechanism for the formation of the tubular morphology.

AS-TuP20 Effect of Annealing TiN/Al₂O₃ Nanofilms Grown on InGaAs. O. Ceballos-Sanchez, A. Sanchez-Martinez, M.O. Vazquez-Lepe, CINVESTAV-Unidad Queretaro, Mexico, P. Lysaght, SEMATECH, A. Herrera-Gomez, CINVESTAV-Unidad Queretaro, Mexico

III-V compounds are candidates to replace Si as the semiconductor in complementary metal-oxide-semiconductor (CMOS) devices.¹ The extensive research for over 40 years in the field of III-V semiconductors reflects the efforts that have been made to find new materials that meet the technological needs. InGaAs is one of the most promising compounds because of its high electron mobility and flexible bandgap as compared to Si.² However, one difficulty associated to III-V semiconductors is the lack of high-quality and thermodynamically stable gate dielectric insulators that passivate the interface. Growing Al₂O₃, HfO₂ and ZrO₂ by atomic layer deposition (ALD) on InGaAs or III-V semiconductors have shown the removal of native oxide and the passivation of the high-*k*/III-V interface.³ However, the high temperatures (~850°C) required for the activation of some dopant in the device induce structural changes that degrade the properties of the interface.⁴ The appearance of oxides, defects or even the diffusion of atoms within the material are issues that primarily affects the device performance. The poor ultimate resolution achieved with some of the characterization techniques traditionally employed for the assessment of the chemical depth profile of thin films limits the quantitative analysis of the structure and composition of the films. In this work we present an analysis by angle-resolved x-ray photoelectron spectroscopy (ARXPS) of TiN/Al₂O₃/In_xGa_{1-x}As nanofilms with different thermal treatments (no-annealing, 500 °C for 2 min, and 700 °C for 10 s). The purpose of the study was to investigate possible reasons of the interface degradation. Through a self-consistent approach based on a multilayer model (MLM), a quantitative study was performed for the composition and thickness of the TiN/Al₂O₃/InGaAs nanofilms. The results clearly show that indium diffuses towards the metal layer as a consequence of heat treatments, suggesting a possible failure mechanism. [1] Han Zhao, Jeff Huang, Yen-Ting Chen, Jung Hwan Yum, Yanzen Wang, Fei Zhou, Fei Xue, and Jack C. Lee, Appl. Phys. Lett. **95**, 253501 (2009). [2] F. S. Aguirre-Tostado, M. Milojevic, C. L. Hinkle, E. M. Vogel, R. M. Wallace, S. McDonnell, and G. J. Hughes, Appl. Phys. Lett. **92**, 171906 (2008). [3] Y. Xuan, H.C. Lin, and P.D. Ye, Appl. Phys. Lett. **88**, 263518 (2006). [4] Y. Xuan, P.D. Ye, and H.C. Lin, Appl. Phys. Lett. **89**, 132103 (2006).

AS-TuP21 Comparison between the Continuous and Discrete Model to Assess the Thickness of SiO₂ Layers on Si with XPS Data. M.O. Vazquez-Lepe, P.G. Mani-Gonzalez, A. Mendoza-Galvan, A. Herrera-Gomez, Cinvestav Queretaro Mexico

X-ray Photoelectron Spectroscopy (XPS) is a valuable tool for assessing the thickness of surface layers in the 0 to 8 nm range. The prediction of a core-level XPS signal from a solid requires assuming a specific volumetric distribution of such core levels. Since the core levels are spaced close to the atomic nucleus, a possible approximation is to model their volumetric distribution as a sum of delta functions at the atomic sites. Another approach is to consider that the source of the photoelectrons is uniformly distributed within the volume of the solid. The latter is called the *continuous approximation* (CA) and the former the *discrete approximation* (DA). The CA is widely employed; it leads to an expression for the XPS signal proportional to $c\lambda \sin \alpha$, where c is the volumetric density, λ is the effective attenuation length, and α is the take off angle. The DA applied to crystalline structures leads to an expression proportional to $s[1 - \exp(-a/(\lambda \sin \alpha))]^{-1} \exp(-a/(2\lambda \sin \alpha))$, where a is the spacing of the atomic planes parallel to the surface, and s is the atomic plane surface concentration ($s/a = c$) [1]. When $a/\lambda \ll 1$, the DA expression reduces to the corresponding to CA. Applying the DA to amorphous materials requires defining an "effective" or "average" atomic spacing (a_e) and surface concentration (s_e). In this paper we compare the differences on the thickness of silica layers on Si[001] calculated with these two approaches. The analysis was done by employing XPS data at one angle or at various angles (ARXPS). The samples employed were thermally grown silica at 800 °C for 16 s, 75 s, 145 s, 212 s and 7 min. The results are also compared to more standard methods [2], such as that employing the parameter R (ratio of the Si 2p XPS intensities for clean Si and thick SiO₂). The thickness of the silica layers were also assessed from Transmission Electron Microscopy (TEM) images and correlated to Ellipsometry measurements. It was found that the approach employing the DA and various angles better reproduced the TEM measurements.

[1] "Self consistent ARXPS analysis for multilayer conformal films with abrupt interfaces." A. Herrera-Gomez. Internal Report 2007 (<http://www.qro.cinvestav.mx/~aanalyzer/arxpsAnalysisSharpInterfaces.pdf>)

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AS-TuP22 Electrical and Surface Studies of the High-*k* Gate Dielectrics Al₂O₃, HfO₂, and Al_xHf_{1-x}O₂ on Silicon via Atomic Layer Deposition. S. Hogan, G. Hernandez, R. Candler, S. Franz, Y.S. Lin, UCLA

As the demand for high speed electronics remains ever increasing, the dimensions of MOSFET technology are continuously scaled down to the smallest possible levels. Traditional gate dielectrics such as SiO₂ are unable to effectively stop electron tunneling from degrading device performance at thicknesses below 1-1.2 nm. We propose using high dielectric materials instead, which can effectively limit leakage current and have a band gap close to SiO₂. This study will focus on the dielectrics Al₂O₃, HfO₂, and Al_xHf_{1-x}O₂ deposited using ALD. Several ratios of aluminum and hafnium in the Al_xHf_{1-x}O₂ compound will be investigated to find a level that maximizes both electrical and physical properties of the film. The electrical properties of each dielectric will be characterized by XPS, AFM, spectroscopic ellipsometry, and by taking IV and CV measurements of fabricated transistors and capacitors. We will also investigate the effects of different annealing and deposition temperatures on the interface by TEM.

AS-TuP23 Enhanced Green Emission from UV Down-Converting Ce³⁺-Tb³⁺ Co-Activated ZnAl₂O₄ Phosphor. K.G. Tshabalala, University of the Free State, South Africa, S. Cho, J. Park, Korea Institute of Science and Technology, Republic of Korea, H.C. Swart, O.M. Ntwaeaborwa, University of the Free State, South Africa

Ce³⁺-Tb³⁺ co-activated ZnAl₂O₄ nanocrystal phosphors were prepared by a solution combustion method using urea (CH₄N₂O, 99.0–99.5%) as a fuel. The samples were annealed at 700°C for 4 hrs, in a tubular furnace, in a reducing atmosphere containing a mixture of 4% H₂ and 96% N₂. The X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM) data showed that a well known cubic normal spinel structure of ZnAl₂O₄ was crystallized. In addition, the HRTEM data showed that the particles were spherical with some degree of faceting. Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) were used respectively to analyze the chemical composition of the phosphors and electronic states of individual elements. The XPS data demonstrated that there was structural readjustment of ZnAl₂O₄ from normal to spinel inversion due to annealing. An enhanced down-converted green emission associated with the ³D₄→⁷F₅ transitions of Tb³⁺ was observed at 543 nm from the ZnAl₂O₄:Ce³⁺, Tb³⁺ powders with different concentrations of Ce³⁺ and Tb³⁺. It was confirmed from the fluorescence decay data that the enhancement was due to energy transfer from Ce³⁺ to Tb³⁺ ions. Possible mechanism of UV down-conversion will be discussed. In addition, cathodoluminescence (CL) intensity degradation was evaluated for possible application of this material as a green emitting phosphor in field emission displays.

AS-TuP24 Characterization of Al_xGa_{1-x}N Thin Film Light Emitting Diode (LED) Device by Spectroscopic Ellipsometry. K. Uppireddi, L. Yan, HORIBA Scientific

The demand for efficient energy usage for lighting at industry viable production costs catalyzing the rapid growth of global LED market. LED lighting is widely in use from LED-backlit TVs to solid-state lighting. The wall-plug efficiency, which characterizes its performance depends on the design and material properties of thin film LED structure. The accurate determination of thickness and composition of the well and barrier layers is desired for quality control in the production. The Sapphire/AlN/Al_xGa_{1-x}N structure was characterized using a phase modulated spectroscopic ellipsometer (PMSE) at an angle of incidence of 70 degree across the spectral range 0.6-6.5 eV. Using a three layer structure we accurately modeled the thickness of the layers in the spectral range from 0.6 to 4.5 eV and Al_xGa_{1-x}N optical constants. The PMSE delivers both unique performance and proven reliability for on-line quality control of production process.

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