

Applied Surface Science

Room: Hall D - Session AS-ThP

Applied Surface Science Poster Session

AS-ThP1 Formation of Pt, Rh, and Pd Nanoclusters on a Graphene Moire Pattern on Cu(111). *Esin Soy, Z. Liang, M. Trenary*, University of Illinois at Chicago

Formation and growth of Pt, Rh, and Pd nanoclusters on a graphene covered metal substrate has been investigated by ultrahigh vacuum scanning tunneling microscopy (UHV-STM). For this purpose a graphene film was formed on the Cu (111) surface by the decomposition of ethylene at high temperatures. According to our results, isolated graphene islands were successfully grown on the Cu surface with different periodicities. Different rotational domains were observed as a result of weakly coupled Cu and graphene caused by the low C solubility in Cu. The most prevalent moire patterns have periodicity of 2.2, 4 and 6.6 nm with rotational angles of 0° and 1.4°, and 37°. Subsequently, nanoclusters were formed at room temperature on the template of a graphene moire pattern formed on Cu (111) surface. As confirmed by the height and size profiles, Rh and Pt clusters display similar planar structures with an average height of about 0.4 nm and average diameter of about 10 nm. The size and distribution of the metal clusters on the two types of Moirés seem to be different. The clusters on the smaller Moiré pattern show a narrow size distribution in both diameter and height. Additionally, these nanoclusters are found to be relatively stable and only undergo agglomeration at relatively high temperatures. These results demonstrate that the metal-C and metal-metal interactions may play a significant role in the cluster formation and it is possible to fabricate finely dispersed metal nanoclusters on the moire structure of graphene covered Cu (111).

AS-ThP2 Valence Band Offsets of Two Rare Earth Oxides on Al_xGa_{1-x}N (0 ≤ x ≤ 0.67) as Measured by Photoelectron Spectroscopy. *Michael Brumbach, A. Allerman, D. Wheeler, S. Atcity, J. Ihlefeld*, Sandia National Laboratories

Preparation of high quality gate oxides on wide bandgap semiconductors is a challenge for realizing efficient high performance devices. For GaN electronics there are a limited number of compatible oxides that have a sufficiently large bandgap to minimize electrical leakage. In this work, reactive molecular beam epitaxy was used to deposit rare earth oxides, Gd₂O₃ and La₂O₃, on GaN substrates. For Gd₂O₃, the valence band offset was tuned by altering the composition of the Al_xGa_{1-x}N substrate. Thin films were characterized using reflection high-energy electron and X-ray diffraction and valence band offsets were determined via X-ray photoelectron spectroscopy.

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AS-ThP3 Surface Electronics of Individual Si-doped GaN Wires Studied by Synchrotron-Radiation XPEEM Spectromicroscopy. *Olivier Renault, N. Chevalier, J.W. Morin*, CEA-LETI, France

Heavily Si-doped GaN wires are at the basis of innovative LEDs used in advanced solid-state lighting. Understanding how silicon incorporation influences the electronic properties and the measured electrical characteristics of recently emerged very high-conductivity GaN wires [1] is of prime importance for future device optimization.

Here, we have implemented photoemission microscopy with synchrotron radiation (XPEEM) [2] and scanning Auger nanoprobe microscopy (SAM) [3] to investigate the incorporation of Si at the surface of individual GaN wires of 2 μm diameter and the local work function. The high-resolution Si2p micro-spectra evidence complex incorporation of Si pointing on intentional (Si substitution in Ga sites) and un-intentional doping (Si substitution in N-vacancies). By combining elemental analysis from SAM and XPEEM core-level results, we can quantitatively discriminate these two contributions to the doping. Next, we have studied the influence of illumination flux on both the work function and Ga3d binding energies, the strong variations of which evidence surface band bending through the surface photovoltage effect.

This work was carried out at the NanoCharacterization Platform (PFNC) of MINATEC.

AS-ThP6 Characterization of Nanostructured Cu-Zn Oxides Used for Photocathodic Water Splitting. *Sankar Raman, J.F. Moulder*, Physical Electronics Inc., *S. Banarjee*, Washington University, St. Louis, *Y. Myung, H. Im, J. Park*, Korea University, *P. Banarjee*, Washington University, St. Louis

Metal alloys can be efficiently exploited, via controlled fabrication steps, to create mechanically robust and adherent, mixed metal oxide films with tunable photoelectrochemical (PEC) properties. Brass, an alloy of Cu and Zn is an inexpensive source of semiconducting Cu₂O, CuO and ZnO, which have all been used separately as photo-cathodes or photo-anodes respectively for solar water splitting. However, thermodynamics and free energy change predicts a prevalence of ZnO formation when brass is oxidized. We have co-fabricated Cu and Zn oxides to form a highly adherent, mixed metal oxide surface and investigated the relationship between structure property and performance in a PEC cell.

Structural and chemical characterization of the oxide layer was accomplished using an SEM and the PHI X-Tool Scanning XPS microprobe. SEM results show the presence of CuO nanowires interspersed with ZnO fibers and high energy resolution XPS provides detailed chemical state information for Cu and Zn on the surface as a function of sample treatment.

This study indicates that the thermal oxidation of metal alloys can lead to formation of highly interspersed, mixed oxide phases forming novel heterojunctions for use as economical and manufacturing-scalable energy harvesting devices.

AS-ThP8 Impact of a Mixed Oxide's Surface Composition and Structure on Its Adsorptive Properties: The Case of the α-(Fe,Cr)₂O₃(0001) Surface. *M.A. Henderson, Mark Engelhard*, Pacific Northwest National Laboratory

Characterization of an α-(Fe_{0.75},Cr_{0.25})₂O₃(0001) mixed oxide single crystal surface was conducted using x-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), low energy electron diffraction (LEED) and temperature programmed desorption (TPD). After sputter/anneal cleaning in ultra-high vacuum (UHV), the mixed oxide surface became terminated with a magnetite-(111) structure based on the presence of (2x2) spots in LEED and Fe²⁺ in XPS. The composition of the surface was close to that of M₃O₄ based on XPS, with the metal (M) content of Fe^{2+/3+} and Cr³⁺ being close to 1.4:1, despite the fact that the film's bulk was 3:1 with respect to the metal cations. The enrichment of the surface with Cr was not altered by high temperature oxidation in UHV, but could be returned to that of the bulk film composition by exposure to the ambient. Adsorption of various probe molecules (NO, O₂, CO₂ and H₂O) was used to identify the active cation sites present in the (Fe,Cr)₃O₄(111) terminated surface. Although XPS and SIMS both indicated that the near-surface region was enriched in Cr³⁺, no adsorption states typically associated with Cr³⁺ sites on a -Cr₂O₃ single crystal surfaces were detected. Instead, the TPD behaviors of O₂ and CO₂ pointed toward the main active sites being Fe²⁺ and Fe³⁺, with O₂ preferentially adsorbing at the former and CO₂ at the latter. NO was observed to bind at both Fe²⁺ and Fe³⁺ sites, and H₂O TPD looked nearly identical to that for H₂O on the Fe₃O₄(111) surface. Competition for adsorption sites between coadsorbed combinations of CO₂, O₂, H₂O and NO corroborated these assignments. These results indicate that the surface composition of a mixed oxide can vary significantly from its bulk composition depending on the treatment conditions. Even then, the surface composition does not necessarily provide direct insight into the active adsorption sites. In the case of the (Fe,Cr)₃O₄(111) termination of the α-(Fe_{0.75},Cr_{0.25})₂O₃(0001) surface, Cr³⁺ cations in the near-surface region appear to be fully coordinated and unavailable for adsorbing molecules.

AS-ThP9 Analysis of Metal Particles by Proximal Excitation of Al and Mg Kα X-rays. *C.F. Mallinson, James Castle*, University of Surrey, UK

In preliminary work [1] we have shown that use of an aluminium substrate to support a distribution of copper particles enables their characteristic photoelectrons to be observed within the Auger electron spectrum generated by an incident electron beam. This observation raises the possibility of the use of chemical shifts and the corresponding Auger parameter to identify the chemical states present on the surface of individual sub-micrometer particles within a mixture. In this context, the technique has an advantage in that, unlike conventional Auger electron spectroscopy, the electron beam does not dwell on the particle but on the substrate adjacent to it. Given the importance, for both medical and toxicological reasons, of the surface composition of such particles we have continued to explore the potential of this development.

In this contribution, we show that proximal excitation of x-rays is equally successful with magnesium substrates: In some regions of the XP spectrum the much larger Auger peaks generated by the electron beam can cause inconvenient clustering of Auger and photoelectron peaks. As in conventional XPS, the ability to switch between Al and Mg sources is useful in such situations. In this context, we have extended the studies to iron and nickel particles where we show that use of Al or Mg substrates, as necessary, can make a contribution to clear identification of individual components in the Fe and Ni 2p peaks.

For this development in electron spectroscopy to achieve its full potential it is necessary to optimise the beam conditions used to generate the local x-ray to give good selectivity of a given particle. Measurements made in support of this will be given. Of greater concern is a possible problem of local heating associated with x-ray generation. We continue to explore this problem and report some progress in minimising heating of the particle whilst maintaining the particle selectivity that is central to this exciting development.

References

1. J. E. Castle, R.Grilli and C.F. Mallinson, "XPS Analysis of Small Particles by Proximal X-Ray Generation" *Surface and Interface Analysis*. DOI 10.1002/sia 5452 (2014)

AS-ThP10 XPS Sputter Depth Profiling of Organometallic Multilayer Materials Using Massive Argon Cluster Ions, Simon Hutton, Kratos Analytical Limited, UK, *T. Bendikov,* Weizmann Institute of Science, Israel, *W. Boxford, SC. Page, J.D.P. Counsell,* Kratos Analytical Limited, UK

Thin polymer films are found in an enormous range of devices and have many applications from use in semi-conductors, displays and solar cells to corrosion protection and packaging. New ion sources such as the multi-mode Ar gas cluster ion source (GCIS) have revolutionised the study of such organic thin films by depth profiling with techniques such as X-ray photoelectron spectroscopy (XPS). As reported elsewhere the chemical composition of organic thin films may now be determined as a function of depth by a combination of XPS analysis and etching using massive Ar ions.

In this study we present results from XPS gas cluster depth profiling of multi-layer organometallic thin films. The multi-layer structures are formed by sequential immersion of a pyridine-terminated template layer on silicon or ITO-coated glass substrates.

AS-ThP11 XPS of Liquids: Chemical Bonding in Ionic Liquids and on Tribo-Films Formed on Cast Iron, Harry Meyer, J. Qu, H. Luo, W. Barnhill, Oak Ridge National Laboratory

Parasitic friction in internal combustion engines accounts for 10-15% of the nearly 7 billion barrels of oil consumed by cars and trucks in the United States. Recently a new group of oil-miscible ionic liquids has been developed as next-generation lubricant additives. Among the many positive attributes of these IL-additives are thermal stability, excellent wettability, non-corrosive, and most importantly, they possess effective anti-scuffing/anti-wear and friction reduction characteristics. Since the idea of using ionic liquids (ILs) as lubricants was raised in 2001, many studies have been conducted in this area and results have demonstrated superior lubricating performance for a variety of ILs. It is widely believed that a protective tribo-boundary film is formed on the contact area by tribochemical reactions between the metal surface and the IL during the wear process and, as a result, reduces friction and wear. However, the study of this critical boundary film in the literature has been limited to two-dimensional topography examination and chemical analysis from the top surface. Several ionic liquids have been evaluated in both bench and engine tests at ORNL and have shown superior wear protection compared to conventional anti-wear additives. In this poster, two IL ([N888H][DEHP] and [P8888][DEHP]) have been used in scuff tests of cast iron samples (pin-on-disk arrangement) and are compared with zinc dialkyldithiophosphate (ZDDP), the most common anti-wear additive. X-ray photoelectron spectroscopy (XPS) was first used to examine chemical bonding in the ionic liquids and the ZDDP in their *liquid state*. This is possible due to the extremely low vapor pressure exhibited by these materials (including ZDDP). The scuff tests produce tribo-films on the cast iron samples. XPS depth profiling is used to determine the composition as a function of depth for these tribo-films. Chemical bonding within the tribo-film is compared and contrasted to the photoemission results obtained on the liquid forms of the IL's and ZDDP.

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AS-ThP12 X-ray Photoelectron Spectroscopy for Electronic Structure and Valence Information, R.G. White, Thermo Fisher Scientific, UK, *Thomas Levesque,* Thermo Fisher Scientific

X-ray Photoelectron Spectroscopy (XPS) is well known for its surface specificity and chemical selectivity. By studying the small binding energy shifts of core level spectra, the analyst may identify the chemical bonding environments of elements present in the surface. When electronic structure or valence information is required, however, many analysts will turn to Ultraviolet Photoelectron Spectroscopy (UPS). There have been many publications in the literature which demonstrate that XPS can also provide electronic and valence information, ranging from work function measurements to valence bonding information.

This work demonstrates the utility of XPS for such measurements and compares results from the same sample set using the complementary techniques of XPS and UPS.

AS-ThP13 Mapping Chemical and Mechanical Property Degradation in PV Modules, Katherine Stika, C.S. Westphal, DuPont Central Research and Development, *J. Kapur,* DuPont Packaging & Industrial Polymers, *R.G. Raty, J. Li,* DuPont Central Research and Development, *J. Kopchick, W. Gambogi, B. Hamzavjehtrany, A. Bradley,* DuPont Photovoltaic Solutions, *J.R. Marsh, B. Foltz,* DuPont Central Research and Development

An understanding of material interactions and degradation pathways in both fielded modules and modules used for accelerated testing is important for photovoltaic (PV) materials specification. As part of the effort to build this understanding, a suite of destructive and non-destructive testing protocols has been developed to compare material performance and reliability under the stresses of different service environments.

This presentation will describe our recent experience mapping the physical and chemical changes observed in degraded PV modules. Examples will include: a) the application of Laser Ablation-Inductively Coupled Plasma-Mass Spec (LA-ICP-MS) for the study of ion migration pathways in encapsulants after PID (Potential Induced Degradation); b) Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) to follow chemical changes in cells extracted from modules following PID and Damp Heat exposure; and c) NanoHardness testing (NHT) to map mechanical property differences in backsheet structures removed from PV modules after field exposure.

AS-ThP14 Surface and Interface Studies of Flexible Front Sheets for PV Modules, Lei Zhang, N.J. Glassmaker, B.B. Sauer, DuPont Central Research and Development

To develop the next generation flexible front sheets for photovoltaic (PV) modules, FEP, a tetrafluoroethylene/TFE copolymer with ~10wt% hexafluoro propylene, has shown great promise due to its low refractive index and superior properties in light transmission. The chemical and photochemical inertness of FEP make it an ideal candidate for PV front sheets; FEP is expected to produce approximately ~1.5% to ~5% improvement in module power output over incumbent glass or poly(co-ethylene-TFE) (ETFE) front sheets.

Because FEP is a per-fluorinated polymer, the grand challenge in the development process is to achieve good adhesion between the FEP film and the underlying poly(co-ethylene-vinyl acetate) (EVA) encapsulant layer. The adhesion of glass and ETFE to EVA has been demonstrated to be durable to environmental effects. However, untreated FEP film has poor adhesion to EVA, especially after accelerated weathering test conditions at elevated temperature and humidity. In order to exploit the advantages that FEP can offer for improved module efficiency, we have developed a multi-step treatment process to modify FEP surfaces for enhanced adhesion of FEP to EVA. Integrated analytical techniques including XPS, contact angle, SEM, and others were applied to characterize the complex surfaces and interfaces of the modified fluoropolymer surfaces. These analytical results have enabled us to better understand the treatment induced functionality on the FEP surfaces, especially the possible mechanism and the locus of failure at the FEP-EVA interface. This presentation will focus on the studies of the modified FEP-EVA surfaces/interfaces and their correlation with adhesion performance.

AS-ThP15 Multi-technique Surface Analysis of Catalytic Systems with XPS, ISS and UPS, Bill Sgammato, Thermo Fisher Scientific, UK

Characterization of catalytic systems benefits from analysis with multiple surface analysis techniques. X-ray Photoelectron Spectroscopy (XPS), for example, is the ideal technique for identifying different chemical species present within the top 10nm of a catalyst surface, but if the elemental composition of the top monolayer is to be investigated then Ion Scattering Spectroscopy (ISS) is the preferred analytical technique. Additionally, if the surface electronic structure can be analyzed, using Ultraviolet Photoelectron Spectroscopy (UPS), then it may be possible to correlate catalytic activity

with electronic structure enabling the analyst to identify the chemical species and active sites responsible for catalytic reactions.

This work demonstrates how a single, multi-technique surface analysis system can be used to comprehensively characterize a catalytic system. XPS, ISS and UPS data is presented.

AS-ThP16 Multifunctional Ultra-High Vacuum Apparatus for Studies of the Interactions of Chemical Warfare Agents on Complex Surfaces, *Wesley Gordon*, U. S. Army Edgewood Chemical Biological Center, *E.M. Durke*, Excet, Inc., *A.R. Wilmsmeyer*, Augustana College, *J.R. Morris*, Virginia Tech

A fundamental understanding of the surface chemistry of chemical warfare agents is needed to fully understand the interaction of these toxic molecules with militarily relevant materials. Knowledge of the surface chemistry of agents can be applied to the creation of next generation decontaminants, reactive coatings, and protective materials for the warfighter. Here, we describe a multi-functional ultra-high vacuum instrument for conducting comprehensive studies of the adsorption, desorption, and surface chemistry of chemical warfare agents on model and militarily relevant surfaces. The system applies reflection-absorption infrared spectroscopy, x-ray photoelectron spectroscopy, and mass spectrometry to study adsorption and surface reactions of chemical warfare agents. Several novel components have been developed to address the unique safety and dosing issues that accompany the research of these toxic, often very low vapor pressure, compounds. Equipment and methods applied in order to safely work with chemical warfare agents will be detailed.

AS-ThP17 A New Transfer Vessel to Facilitate the Characterization of Air-Sensitive Materials, *Richard White*, *T.S. Nunney*, Thermo Fisher Scientific, UK, *H.M. Meyer*, Oak Ridge National Laboratory

Analysing key components of technologically significant devices such as OLED displays, Li-ion batteries and catalyst materials can present challenges to the surface analysts. Amongst the most critical issue is the air sensitivity of these materials. Small amounts of oxygen or water vapour can cause radical changes in the material, ultimately affecting the analysis results and leading to uncertainty in the validity of any conclusions drawn.

Transfer from the preparation environment to the instrument requires the samples to be loaded into a container that can be unloaded into vacuum in the analysis instrument without exposure to the ambient atmosphere. In this presentation we will show results obtained using a new transfer vessel, designed to make the introduction of samples into the vacuum system more automated. Data has been collected from samples covering a range of application areas in order to validate the system, and this will be used to illustrate the benefits of the design.

AS-ThP18 Large-Area Secondary Ion Mapping: An Essential Component of Industrial Problem-Solving, *Kathryn Lloyd*, *J.R. Marsh*, DuPont Corporate Center for Analytical Sciences

Secondary Ion Mass Spectrometry (SIMS), carried out with liquid metal primary ion sources and time-of-flight mass analyzers, has long been recognized as a means of obtaining lateral distributions of species at the surface via detection of chemically-specific molecular ions. As efforts continue to routinely achieve sub-micron lateral resolution from organic and electrically-insulating samples, it is worth noting that the technique easily lends itself to large-area (millimeters to centimeters) chemical mapping. This capability fills an important niche in the chemical mapping “toolbox” and is relevant to many industrial surface-related problems.

For small-area (less than $500 \times 500 \mu\text{m}^2$) mapping, the primary ion beam optics are (usually randomly) rastered across a pixel array spanning the area of interest, and secondary ion spectral data is collected at each pixel. In the simplest implementation of large-area mapping, the sample stage is moved in regular (essentially large pixel) intervals under an optically-stationary primary ion beam. A more optimal approach is to combine both small-area ion beam rastering with stage rastering in a so-called “patch” configuration.

These large-area mapping acquisitions typically take 30 minutes. Coupled with multivariate analysis, they provide a chemical view of the surface not easily obtainable from other techniques. Examples shown will include optimization of anti-stat coating, understanding fabric color streaking, and assessment of printing uniformity.

AS-ThP19 In Situ Ar Plasma Cleaning of Samples Prior to Surface Analysis, *Vincent Smentkowski*, *H. Piao*, General Electric Global Research Center, *C.A. Moore*, XEI Scientific

The surface of as received samples is often contaminated with adsorbed layers of hydrocarbons. These surface contaminants can attenuate or mask underlying species of interest, inhibiting or compromising accurate analysis. *In-situ* ion beam sputtering is often used to remove the outer layer of a sample surface and thus remove contaminants, however this erosion process

is inherently destructive and can alter the surface of interest. Moreover there are also many materials that can not be cleaned using monoatomic ion beam sputtering as the material(s) may decompose and deposit a layer of fragments onto the outer surface of the material to be analyzed. Recently gas cluster ion beams (GCIB) have been developed^{1,2}, which allows for depth profile analysis of organic layers with minimal degradation³ (and references therein). GCIBs have also been used for low damage surface cleaning^{4,5,6}. A non line-of-sight protocol which is able to clean large (mm or greater) areas is desired. We recently demonstrated that ambient air plasma processing can be used to clean the outer surface of samples⁷, however ambient air plasma treatment can result in oxidation of the material. In this presentation we report our first attempts at *in-situ* plasma cleaning of samples using Ar prior to XPS and ToF-SIMS analysis. We compare Ar plasma cleaning with air plasma cleaning, and report key findings.

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AS-ThP20 Discrete Distribution Profile Model for Characterization of Ultra-Thin Surface Films, *Tatyana Bendikov*, *T. Toledano*, *H. Cohen*, Weizmann Institute of Science, Israel

Accurate characterization of ultra-thin surface films is a basic requirement for the successful development of the electronic devices. For example, electrical transport measurements in molecular electronics, often consisting of ultra-thin films, are extremely sensitive to the quality of the films and their associated interfaces. As an experimental technique, X-ray Photoelectron Spectroscopy (XPS) is uniquely suited for the direct characterization of thin films in terms of layer thicknesses, elemental composition and, frequently, the depth-distribution profile of elements across the film. However, interpretation of the raw experimental data requires a reliable theoretical modeling of the photoelectron attenuation; a mechanism that is usually addressed by considering a continuum medium with a phenomenological attenuation parameter. Such models impose severe limitations when self-assembled molecular layers (SAMs) are to be analyzed. In SAMs studies, calculations based on a Discrete Distribution Profile (DDP) are necessary for a proper accounting of atoms situated at the specific locations along the molecular backbone.

In this work, 1-undecane, 11-chloro monolayer deposited on Si substrate was used as a model system. XPS intensities of carbon, chlorine, oxygen and silicon were measured and their components (C_{C1} , C_{Si} , Si_{Ox} , Si_C) were quantified using curve fitting analysis. The intensity ratios (C_{tot}/Cl , C_{tot}/C_{C1} , C_{tot}/C_{Si} , C_{tot}/Si_C , C_{Si}/Si_C) were then compared to DDP calculated ratios, yielding excellent agreement between experimental and calculated values. The detailed agreement points to the high quality of the studied layers and, more generally, supports the validity of the DDP model as a tool for thin films characterization.

AS-ThP24 Co-solvent Enhanced Zinc Oxysulfide Buffer Layers in Kesterite $Cu_2ZnSnSe_4$ Solar Cells, *Xerxes Steirer*, *R.L. Garriss*, *J. Li*, National Renewable Energy Laboratory, *M. Dzara*, Rochester Institute of Technology, *P.F. Ndione*, *K. Ramanathan*, *I. Repins*, *G. Teeter*, *C.L. Perkins*, National Renewable Energy Laboratory

Thin film solar cells rely upon the efficient transfer of photocharge from the absorbing photovoltaic material to an external circuit via thin buffer junction layers. Problems such as low fill factor and current loss arise when the electron collecting contact (emitter) exhibits a large positive conduction band discontinuity with the absorber. This study shows evidence for one approach to circumvent this problem by taking advantage of electronic defects prominent with chemical bath deposition (CBD) of buffer layers. X-ray and ultraviolet photoelectron spectroscopy (XPS/UPS) of heterojunctions formed between CZTSe and CBD-ZnOS with two different buffer preparations exhibit clear differences in electronic properties yet we observe no discernable differences in composition. Structure of CBD-ZnOS made using the different preparation methods is measured with grazing incidence X-ray diffraction (GIXRD) and also exhibits no discernable

differences in the peak positions or full widths. XPS/UPS derived band energy diagrams are presented for quasi-*in-situ* prepared CZTSe/CBD-ZnOS interfaces with both preparation methods yielding valence band offsets equal to -1.0 eV and conduction band offsets equal to 1.1 eV. However, comparison between water only and a water/dimethyl sulfoxide solvent mixture in device characterization and band offset measurements show increased band bending in accordance with higher n-type carrier density with water as the only solvent. Seemingly incongruous, the more strongly n-type buffer layer performs worse in solar cells and exhibits inflected current-voltage response under one-sun illumination. A proposed electron transport band for these buffer layers that seems to circumvent the large conduction band spike is estimated to have energies about 0.6 eV below the conduction band of the CBD-ZnOS. Hence, these defects appear to enable adequate band-lineup with the low-band gap absorber, CZTSe ($E_g = 0.96$ eV). These findings suggest that cosolvation approaches may allow for the manipulation of the electronic structure of ZnOS and enable a wider range of electronic applications where larger electron affinities are required.

AS-ThP25 Analysis of Metal Nanoparticles by Auger, XPS and TEM, *Wayne Jennings*, Case Western Reserve University, *C.V. Bishop*, The Best Mode Company, *J. Cowen*, Case Western Reserve University, *J.S. Hammond*, *D.F. Paul*, Physical Electronics USA

Nanoparticles of Pd and PdSn are important as catalysts for chemical reactions and metallization of polymeric materials. Metallization applications include nano-circuitry and automotive plating on plastic. Catalytic applications include the Heck and Suzuki reactions and a variety of other coupling reactions (hydrogenation, dehydrogenization and petroleum cracking). A common synthesis route for Pd nanoparticles is reduction of PdCl₂ with stannous compounds. The structure and purity of the resulting particles is critical to their performance. TEM has been used to examine PdSn nanoparticles for their compositional structure. For very small particles, EDS and EELS analyses become difficult due to the expanded excitation volume. Surface sensitive methods have utility for effective characterization of materials of this type. This work demonstrates the utility of scanning Auger analysis in characterization of particles of this type that effectively compliments TEM methods.

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