

Applied Surface Science

Room 117 - Session AS-ThA

Complementary Methods and Industrial Challenges

Moderators: Vincent Smentkowski, GE Research Center, Suntharampillai Thevuthasan, PNNL

2:15pm AS-ThA-1 ASSD Student Award Finalist Talk: Elucidating the Interaction Forces between Surface Nanobubbles and Nanoparticles, Daniela Miano¹, P. Bilotto, CEST GmbH, Italy; M. Valtiner, TU Wien, Austria
Efficient surface cleaning protocols are imperative across diverse industries to ensure product quality and performance. The new direction of nanoelectronics requires surfaces to be cleaned at the nanoscale. In the last decade, surface nanobubbles have been shown to remove nanoparticles from silicon wafers. [1] Nevertheless, the specific surface nanobubble-nanoparticle interaction has not been fully understood, calling for a deeper investigation.

We explore the formation and stability of surface nanobubbles by employing atomic force microscopy (AFM). After solvent/water exchange we characterize them in terms of topography and their interaction in different wettability and environment scenarios (i.e., change in solvent, nanoparticle types, gas concentration, and surface functionalization). The presence of NBs can lead to localize changes in wettability, roughness, and chemical reactivity.

Managing the balance between enhanced cleaning and surface potential is crucial. Over time, this alteration may impact the substrate's integrity or alter its performance characteristics.

Interestingly, we observe the formation of nanoholes, which we interpret in terms of short range forces (DLVO theory) and chemical equilibrium in confinement. The latter takes inspiration from *pressure solution* as described in geology. It helps identify the physical and chemical interactions occurring when nanoparticle detachment from the substrate. [2]

Our research work aims to describe solid-liquid interface, with particular interest to the phenomena correlate the interactions force between surface nanobubble-nanoparticles and surface and nanoparticles-surface. Research on surface nanobubble and the study of their possible application is necessary because there is not a unified vision in the scientific community. The results can impact both the scientific and industrial categories, by addressing respectively unsolved interactions at the nanoscale and upscaling nano-cleaning processes at the macroscale.

[1] S. Yang, & A. Duisterwinkel, A. (2011). Removal of Nanoparticles from Plain and Patterned Surfaces Using Nanobubbles. *Langmuir*, 27(18), 11430–11435. doi:10.1021/la2010776;

[2] K. Kristiansen, M. Valtiner, G.W. Greene, J.R. Boles, J.N. Israelachvili (2011). Pressure solution - The importance of the electrochemical surface potentials. doi:10.1016/j.gca.2011.09.019

2:30pm AS-ThA-2 A Correlative Microscopy Platform for In-Situ AFM-SEM-EDS, Kerim T. Arat, W. Neils, S. Spagna, Quantum Design Inc.

In-situ correlation of AFM-SEM techniques implemented in a highly integrated tool offers the complementary strengths of two different imaging modalities without the inherent complications of sample transfer. This is not only a significant convenience for researchers but also ensures a high confidence in correlation accuracy and eliminates the risk of sample contamination and alteration during the sample transfer.

Previously, we have developed a correlative microscopy platform based on AFM-SEM [1]. These techniques can map the surface in high resolution and the trunnion, with up to 80° tilt capability, allows monitoring of process quality such as tip measurement or monitoring tip sample interaction. However, none of these can measure the elemental composition of the material.

We have extended the capabilities of the correlative platform with an energy-dispersive X-ray spectrometer (EDS) to extract the elemental information from the sample. The spectrometer is based on a state-of-the-art silicon drift detector [2], which provides high energy resolution (< 133 eV, Mn-Kα). Its unique graphene window offers better transmission, especially at the lower energy range, allowing elemental detection down to

carbon. The EDS elemental identification algorithm uses a background subtraction method and compares the resulting spectra to reference datasets based on the NIST database [3]. Both hardware and software integration allow correlation of elemental information with the other imaging modalities that the tool can provide (see the supplementary document) where one can superimpose topography and elemental information.

Integration of the X-ray detector adds a significant analysis capability to AFM-SEM techniques applicable to a diverse range of materials such as metals, alloys, ceramics, and polymers. With this addition of EDS, researchers can obtain in-situ correlation of high-resolution, localized elemental information with high-resolution lateral and vertical topographical information, without the complications of sample transfer.

[1] A. Alipour et al., *Microscopy Today* 31 (2023), p. 17-22. doi: 10.1093/mictod/qaad083

[2] D. E. Newbury and N. W. M. Ritchie, *Journal of Materials Science* 50 (2015), p. 493-518. doi: 10.1007/s10853-014-8685-2

[3] D. E. Newbury and N. W. M. Ritchie, *Scanning Microscopies* 9236 (2014), p. 9236OH. doi: 10.1117/12.2065842

2:45pm AS-ThA-3 Coincident XPS, Raman and SEM Analysis of Additive Manufacturing Devices, Mark Isaacs, University College London, UK; D. Morgan, Cardiff University, UK; A. Leung, K. Kim, S. Bhagavath, University College London, UK

Additive manufacturing processes are a keenly investigated methodology for the preparation of sophisticated devices for a multitude of technologies, including catalysis, electronics and sensors. At the heart of the functionality of these systems often lies the surface and interfacial properties of the resultant materials. In order to develop a holistic understanding of the eventual nature of these devices, and for the complete assessment of favourable printing parameters, oftentimes a multitude of characterisation methods is required. Coincident analysis of surface analysis techniques such as XPS, SEM, REELS and UPS - along with additional complementary techniques such as Raman spectroscopy - permits a wealth of understanding around the physical, chemical and electronic properties of printed tracks and leads to an overall optimisation of system parameters to develop highly specific and tuneable materials. In this work, we study a range of printing parameters for the deposition of MoO₃ tracks onto a copper support - a material with promising applications in the electrocatalytic reduction of CO₂. Using XPS, linked with SEM/EDX via a CISA (Correlative Imaging and Surface Analysis) Workflow and Raman spectroscopy, we investigate a range of printing parameters in order to determine favourable properties for the creation of phase interfaces understood to be active for electrocatalytic applications. Chemical and electronic properties are also investigated through complimentary surface analysis by REELS and UPS.

3:00pm AS-ThA-4 Analysis of Cu-Ag and Ni-Pt High Throughput Survey Results, Kyle Dorman, N. Bianco, R. Kothari, M. Kalaswad, C. Sobczak, S. Desai, J. Custer, S. Addamane, M. Jain, A. Hinojos, F. DelRio, B. Boyce, R. Dingreville, D. Adams, Sandia National Labs

Nanocrystalline thin films feature the potential for enhanced or altered material properties compared to their bulk single crystal counterparts. Recent studies on Pt-Au binary thin films have emphasized the role of grain boundary character in successful solute stabilization of otherwise thermally unstable nanocrystalline systems (C. M. Barr et al., *Nanoscale*, 2021), and means of high-throughput combinatorial synthesis (McGinn, *ACS Comb. Sci.*, 2019) have been developed to complement automated characterization and modern simulation capacity. To further develop our understanding and suite of tools, and to step beyond the most noble alloy into more economically practical material systems, compositional surveys of Cu-Ag and Ni-Pt were performed in search of optimized material properties and greater comprehension of nanocrystalline systems. Facilitated by a fixed substrate and photolithography, a simultaneous co-sputtered deposition of each pair of elements with pulsed DC magnetron methods directing single element sources creates a varied atomic composition across 112 samples on a single 150 mm diameter wafer. A series of such depositions, varying the gun-tilt angle and power at each cathode, allows swift examination of nearly the full range of alloy compositions. Wavelength Dispersive Spectroscopy, Atomic Force Microscopy, X-ray Diffraction, X-ray Reflectivity, sheet resistance, optical profilometry and nanoindentation were employed for automated mapping analysis. The binary collision Monte Carlo program SiMTra (D. Depla et al., *Thin Solid Films*, 2012) assisted with the deposition design to minimize the necessary quantity of sample batches, and enabled analysis of the

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energetic and compositional properties of the wafer at deposition with respect to the resultant hardness, modulus, film density, crystal texture and resistivity. This permits specification of desirable processing conditions in relation to exemplary and underperforming films. Accompanied by exploration of the strengths and weaknesses of the dataset, and the means to improve further such surveys.

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3:15pm AS-ThA-5 Characterization of Functional Surface Modifications in Medical Devices, *Andrew Francis, A. Rafati, A. Belu*, Medtronic, Inc.

Surface modifications provide important functionality for medical devices, such as increased lubricity, improved hemocompatibility, and localized drug delivery. Characterization of these modifications is essential to understanding and controlling their interactions with a patient. Here, the development and characterization of new functional surface modifications for medical devices is reported with several examples shown. In particular, the spatial-chemical distribution and functional testing of a new biomimicry surface modification will be highlighted in combination with key clinical results. A range of analytical techniques (SEM/EDS, TOF-SIMS, XPS, and Raman spectroscopy) and biochemical methods and assays (blood loop model, TAT, etc.) will be discussed.

3:30pm AS-ThA-6 XPS Study of ZrN as a Barrier to Silver Migration in TRISO Fuels, *Jeff Terry*, Illinois Institute of Technology

We have measured simulated TRISO Fuel model structures of SiC and ZrN with and without a 2 nm carbon capping layer. We have used both Sputter Depth Profiling with conventional X-ray Photoemission (XPS) and Ambient Pressure X-ray Photoemission Spectroscopy (APXPS) to explore the reactivity of these layers with both Ag and H₂O. One set of the samples that were depth profiled were measured at room temperature. Another set was annexed to 500 °C and then cooled to room temperature before profiling. The samples measured with APXPS were exposed to 1 mbar of H₂O exposure and annealing up to 500 °C. The exposure was done in a near ambient pressure cell within the XPS system. High resolution scans of the Ag 3d, Zr 3d, O 1s, Si 2p, C 1s and N 1s region were collected and the peaks were fit to identify the chemical species as it is being exposed and annealed. The fitting was performed using our Artificial Intelligence analysis package XPS Neo. This study shows that materials used in TRISO fuel (SiC and ZrN) have a strong reaction to water and high temperature and having a barrier layer of carbon to can effectively prevent oxidation of the materials. The Ag is effectively stopped by the ZrN layer. Adding a layer of ZrN may prevent exposure to workers during shutdowns.

3:45pm AS-ThA-7 Surface Properties of Actinide Dioxide and Their Effect on Reactivity, *Enrique Batista, G. Wang, P. Yang*, Los Alamos National Laboratory

Actinide compounds, especially actinide oxides, play a critical role in many stages of the nuclear fuel cycle. The behavior of these materials under different conditions dictates aspects from crystal growth to disposal of spent fuels, and much of those properties start at the surface. In that way, catalytic reactions that can lead to unstable storage conditions stemming from surface interactions with environmental species. Similarly, the morphology and structure is dictated environmental conditions and the reactivity of the incipient solid to the species present in solution. We have recently been focusing on surface properties induced by the presence of surface defects and surface interactions with environmental and non-environmental molecules. In this presentation we discuss the effect of surface defects in the reactivity and catalytic properties of the different exposed surfaces. Examples of reactions catalyzed by actinide surfaces to be discussed include water oxidation and nitrogen reduction to ammonia. Since these interactions can be deleterious, approaches to prevent them without affecting the desired properties of the material will also be discussed. We present results of these studies for a series of actinide dioxides (AnO₂).

4:00pm AS-ThA-8 Degradation Analysis of Bitumen Using XPS, *Nirmalya Karar*, National Physical Laboratory, India; *S. Kar*, CSIR-CRRI, India

In this presentation, we shall discuss about the degradation of bitumen as observed using XPS. It was initially thought that XPS could not be done on such samples as it is an oil based product with a non-negligible vapor pressure. We use 2 different bitumen grades for our analysis. Road Engineers denote them as VG-10 and VG-30 respectively. Different old used bitumen samples of known provenance were extracted from Indian roads for this analysis and compared with control samples obtained from an

Indian oil company. The primary elements present were C (C1s), S (S2p) and O (O1s). N(1s), Pb (Pb4f) or Ni (Ni2p) were not seen in these samples. We shall show how these elemental peaks change under different conditions as compared to the control samples. The significance or importance of our studies on the local economy is due to the tropical weather conditions present in South Asia, e.g. high rainfall, high temperatures, heavy sunshine for most parts of the year, heavy traffic loads, and large differences in daily maximum and minimum temperatures on many parts of the country, leading to relatively faster degradation of bitumen-asphalt based roads, as opposed to similar roads in colder countries. So, a road construction methodology that may be suitable and quite successful in moderate or cold climatic conditions may not necessarily be as successful for tropical countries.

4:15pm AS-ThA-9 High-Efficient Bifacial Ge-incorporated Sb₂Se₃ Photovoltaic Devices Enabled with Cu₂O Back Buffer, *Sanghyun Lee, K. Price*, University of Kentucky

Antimony Selenide (Sb₂Se₃) thin-film solar cells have gained attention as third-generation photovoltaic devices with promising properties. With a bandgap of 1.1 eV, it has a high absorption coefficient at visible light (>10⁵ cm⁻¹), good carrier mobility (<15 cm²/Vs), long carrier lifetime (<67 ns). Additionally, the simple binary nature of Sb₂Se₃, along with its high vapor pressure and low melting point, makes it suitable for various cost-effective deposition techniques. The versatility of Sb₂Se₃ thin-films has led to extensive research into their composition and the integration of different elements for a range of uses. Specifically, incorporating Germanium into Sb₂Se₃ (Ge-Sb₂Se₃) has shown promise as an effective polycrystalline absorber, especially when the Germanium content is maintained below 15%.

Enhancing the performance of polycrystalline Sb₂Se₃ devices could be achieved by capturing light on both the front and back sides through a bifacial device design. However, the advancement of bifacial devices in thin-film photovoltaic technologies has been limited due to their short carrier lifetimes (<100 ns), especially when compared to polysilicon-based devices. For example, the highest efficiencies recorded for rear-side illumination are 9.2% for CIGS, 8.0% for CdTe, and 9.0% for Kesterite solar cells. Research into optimizing bifacial photovoltaic structures is ongoing and a key is to select a transparent back buffer layer and a transparent conducting back contact, adjusting the thickness and doping concentration to enhance the bifaciality factor (efficiency ratio of rear-to-front illumination).

In this study, we have investigated the feasibility of developing bifacial Ge-Sb₂Se₃ devices, beginning with the creation of Ge-Sb₂Se₃ absorber thin films and proceeding to assessing their optical characteristics. These characteristics were then employed as critical input parameters for the computational modeling and simulation of the bifacial device structure. Utilizing in-house MATLAB modeling suites connected to external Sentaurus TCAD simulators, we introduced innovative bifacial device designs aimed at enhancing device efficiency and further refined these models by adjusting a set of parameters. After carefully selecting a Cu₂O back buffer layer, the best efficiency of front-side illumination is 19.7 %, and Voc is 744.4 mV, Jsc is 40.14 mA/cm², and FF is (66.1 %). For the rear-side illumination, efficiency is 13.0 %, Voc is 724.5 mV, Jsc is 31.6 mA/cm², and FF is 56.7 %. All in one, the bifaciality factor of Ge-Sb₂Se₃ devices was 66 %.

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