Thursday Evening Poster Sessions, October 24, 2019

Applied Surface Science Division
Room Union Station B - Session AS-ThP

Applied Surface Science Poster Session

AS-ThP1 Hydrogen Generation Eases Safety and Infrastructure Requirements for Efficient and Productive Vacuum Deposition Processes, *David Wolff,* Nel Hydrogen

Hydrogen is frequently employed as a backfill gas during various vacuum coating processes involving metals. Hydrogen plays several roles and provides multiple benefits:

- As a carrier gas and diluent for active gases used to modify substrate surfaces

- As a cleaning and protective agent to clean deposition surfaces and prevent oxidation at high temperatures

- High purity hydrogen is relatively inexpensive, safe and effective in this application when used properly

The major challenge with hydrogen is the storage of hydrogen often required to have a source of pure hydrogen gas. Hydrogen gas for small and medium scale applications is generally delivered from far-away generating facilities and stored at the customer's site in the form of a compressed gas. Storage of hydrogen is closely controlled by national and international code guidelines and local Authorities Having Jurisdiction.

Proton Exchange Membrane (PEM fuel cell technology) hydrogen generation makes it possible to generate hydrogen at production rates and purity levels suitable for scientific and production applications. Most importantly, PEM hydrogen generation produces pure, pressurized, dry hydrogen in a load-following fashion without the need for hydrogen storage.

Poster will outline the code and cost advantages that PEM hydrogen generation can provide for scientific and production hydrogen use in vacuum applications.

AS-ThP2 Progress in Understanding SIMS Spectra from Silicones, *Paul Vlasak, M.L. Pacholski,* The Dow Chemical Company

The unique properties of poly(dimethylsiloxane), also known as PDMS or silicone, have allowed PDMS-based materials to proliferate in modern industry. A huge variety of applications using PDMS have been developed including structural adhesives, release agents, optical components, lubricants, anti-foam agents, and potting agents to name a few. Considering the omnipresence of PDMS in industrial settings along with its low surface energy and tendency to migrate, it comes as no surprise that PDMS is frequently encountered in industrial surface analysis laboratories. Because PDMS is readily detected and easily recognized by its characteristic fragmentation pattern, SIMS is well suited to identifying the presence of silicones on a wide range of materials.

Over the years we have observed variation in the fragmentation patterns and relative intensities of characteristic ions in the SIMS spectra from assorted PDMS-containing materials, however, the structural details that may influence the observed spectra remain poorly understood. In the past, we confirmed that endgroup type and molecular weight of PDMS fluids have a systematic influence on negative ion spectra. In addition, we determined that substrate type and thickness of the PDMS layer also greatly influence the spectra obtained, allowing us to hypothesize that the differing energy distributions and collisional cascades within the films and substrates strongly influence ion yields [1].

Using well-characterized PDMS reference materials spin-coated on a variety of substrates, the effects of cluster ion versus monoatomic ion sputtering will be presented as an extension of our past work. In addition, we previously demonstrated that spectra from a particular PDMS fluid became independent of substrate type as film thickness increased beyond the penetration depth of the primary ions, while current work further explores the sub-monolayer regime. Lastly, using thin films of various PDMS mixtures, investigation of potential layering of PDMS as a function of molecular weight or endgroup type will be presented.

[1] Vlasak, P.R.; Pacholski, M.L. (2018, October) *Differentiating Silicones Using SIMS*; presented at AVS 65th International Symposium & Exhibition, Long Beach, CA.

AS-ThP3 Silicon Wet Etching Using NH4OH Solution For Texturing of Silicon Micro-Channels, *José Alexandre Diniz,* A.R. Silva, UNICAMP, Brazil

This work presents the surface texturing of the horizontal wall of silicon micro-channels (SiMCs) using the NH4OH solution. The micro-channels are obtained on the backside of Si substrates, where the solar cells are fabricated. The micro-channels are used as heat sinks through which fluid will flow, such as water or alcohol. The texturing results in the micro-channels with roughness (in micro-pyramid shape) on horizontal surface. The roughness assists in the dilution of bubbles that can occur inside the fluid, because if the bubble excess occurs into the fluid, this can difficult the transport into the SiMC. The texturing is based on the formation of micro-pyramids with the use of NH4OH (ammonium hydroxide) alkaline solution etching, which is anisotropic. Our NH4OH solution etching can control the size of micro-pyramids on the surface into the SiMC This occurs because the etch rates are different for three [100], [110] and [111] Si crystal planes. The Si etching is due to the presence of the OH- (hydroxyl) in the NH4OH solution that reacts with Si. The micro-pyramids occurs because the (100) mono-crystalline substrates have a lower Si surface density of the plane than the (110) plane. The difference in density causes the etch rate for (100) plane to be greater than (110), which in turn, is greater than for (111). Thus, since it is a surface with lower density is easier penetration of the solution, which facilitates the Si reaction with hydroxyl (OH -). Anisotropic etching is obtained by alkaline solution of monocrystalline Si substrate, with (100) surface orientation. Exposure of [111] crystal plans occurred, forming the micro-pyramids. The obtained values of micro-pyramid height of 770 nm and 920 nm, when compared with a desired micro-channel depth of 200 μm, represent a ratio (between roughness and channel depth) lower than 5%. This ratio is considered suitable to reduce a significant impact on micro-channel performances.

AS-ThP4 Ionic Liquids: Advanced Oil Additives for Lubricating Case-Hardened Titanium Alloys (OD-Ti64), *Harry Meyer III,* H. Duan, W. Li, C. Kumara, Y. Jin, H. Luo, J. Qu, Oak Ridge National Laboratory

Titanium alloys possess many excellent characteristics (corrosion resistance, high fatigue strength and high strength-to-weight ratio) that has led to many important applications in several field (aerospace, bioengineering, automotive, etc.). However, these same alloys have only limited use as tribological materials due to abrasion and adhesion resistance. We previously investigated the use of oxygen-diffused Ti64 (OD-Ti64) and found that, in dry sliding conditions, the oxygen diffusion treatment improved the wear resistance compared to untreated Ti64. OD-Ti64 performed better than untreated Ti64, with respect to wear resistance when a lubricant containing ZDDP because of the formation of a ZDDP-based protective triobfilm.

This study extends these previous investigations by evaluating the use of ionic liquids (ILs) as oil additives to lubricate oxygen-diffusion (OD) case-hardened titanium for improved friction and wear behavior. A base oil for boundary lubrication of an OD-treated Ti-6Al-4V sliding against a steel ball was tested using four oil-soluble ILs used as additives. This poster will present data that will show (1) the ILs improved the friction behavior to various extents; (2) two phosphate ILs clearly outperformed conventional ZDDP; (3) ILs exhibited excellent wear protection suggesting good material-chemical compatibility; and (4) the carboxylate IL protected the OD-Ti surface from any measurable wear. The morphology and chemical composition of the worn surfaces and tribofilms were examined using a combination SEM, TEM, EDS, and XPS.

AS-ThP5 Controlling Surfaced-catalyzed Coupling of Aryl Halides for Preparation of Two-dimensional Covalent Networks, *Margaret Wolf,* C.R. Gerber, R.C. Quardokus, University of Connecticut

Formation and design of two-dimensional carbon-based materials can be controlled through surface-catalyzed reactions of small molecules. We use low-temperature scanning tunneling microscopy (LT-UHV STM) to monitor and characterize the surface-catalyzed reaction of dibromobenzene and dibromobithiophene. The Ullmann-like and Yamamoto-like coupling on

Au(111) lifts the gold herringbone reconstruction and the gold atoms and coupled adsorbate are mobile at 4 K. Annealing results in two-dimensional covalent networks and restores the gold herringbone reconstruction.

AS-ThP6 Characterization of Mineral Associated Organic Matter in Alkaline Soil, *Mark Engelhard*, R. Kukkadapu, T. Varga, R. Boiteau, L. Kovarik, J. Cliff, M. Wirth, A. Dohnalkova, C. Smallwood, D.E. Perea, J. Moran, K. Hofmockel, Pacific Northwest National Laboratory

Warden Soil (alkaline, fine sandy loam) from Prosser, WA was characterized by a suite of spectroscopic and microscopic techniques to gain insights into the nature of mineral-associated soil organic matter (SOM) and its stability under environmental perturbations (e.g., after spiking the soil with siderophores, fluctuating redox conditions, etc.). This approach was undertaken since: a) SOM associated with minerals has been recognized to be relatively stable with respect to biological degradation compared with particulate organic matter (POM), and b) the stability of mineral-OM moieties is primarily a function of interaction between the mineral and OM type, and their physical accessibilities by organisms, oxidants, etc.

Coupled Mössbauer spectroscopy and XRD measurements revealed that ~60-65% of total Fe (5.5 wt.%) in the soil was present in feldspars. The balance of the Fe was primarily partitioned as magnetite, ilmenite, and a suite of nano-Fe(III)-oxides. Various forms of Ca were evident in TEM as: a) "Ca-OM polymers", b) $CaCO_3$ coated with Ca-OM (consistent with XPS results), and c) Ca feldspar. OM-coated magnetite particles were also evident in TEM results. XPS measurements also demonstrated various types of surface organic C (20-25× that of bulk): a) aliphatic and aromatic C-(C-H), such as C-C, C=C, C-H, b) C-(O,N) bonds as in carbohydrates and amines, c) C displaying bonds to oxygen as in aldehydes, ketones, and amides (C=O, O-C-O, O=C-N), and iv) carboxylic C (O-C=O. NanoSIMS results of ^{13}C- and ^{15}N-labeled siderophore-spiked soils showed that Ca-OM phases rather than Fe-OM phases were preferential hosts for siderophores implying weaker but quickly forming interactions were preferentially established and stable enough to exist in calcareous environments. This provides a potential explanation of the lack of pyoverdines/catechols (siderophores) observed in grassland soils, and more broadly demonstrates the importance of adsorption kinetics rather than thermodynamic equilibrium on the fate and preservation of SOM.

AS-ThP7 Atomic Structure Simulation of Nitrogen Supersaturated Austenitic Stainless Steel, *Honglong Che*, M.K. Lei, Dalian University of Technology, China

Low temperature nitriding of Fe-Cr-Ni austenitic stainless-steel forms a nitrogen supersaturated layer that owns a composite property of wear and corrosion resistance. It is widely used in the industry, and nuclear power plant is a very important application for its stringent performance requirements. To understand the nature of this nitrogen supersaturated layer, a serial systematically composition changed Fe-Cr-Ni austenitic stainless steel in three groups are prepared, nitrided and investigated. It is confirmed that the nitrided layers on all the Fe-Cr-Ni austenitic alloys are consistent of duplex structure of outer γ'-Fe N like orderedγ'$_N$ and inner γ$_N$, althougha featureless continuous layer is observed with light-optical microscopy and a gradual decrease in nitrogen content is measured with EPMA when the alloys with a Cr-content over 12 wt. %. Cell model based on Cr-N and Fe-N interaction that considered the atomic construction of octahedral interstice is built that can explain the composition and structure evolution during the alloy composition change. The Cell Model is also used to calculated the average nearest neighbor nitrogen atoms (ANNNA) around Cr and Fe, which well explained the extended X-ray absorption fine structure (EXAFS) experiment results in both as nitrided and denitrided of 304 and 316 stainless steel. It further confirmed the reasonability of Cell Model and revealed the atomic structure of the γ'$_N$ and γ$_N$ phase.

AS-ThP8 Determination of the Number of Layers of a 2D Material by Angle-Resolved Photoelectron Spectroscopy, *P. Tyagi*, University at Albany - SUNY; *Carl A. Ventrice, Jr.*, SUNY Polytechnic Institute

The electronic structure of most 2D materials depends on the number of molecular layers and the stacking sequence between the layers. Therefore, it is important to have a non-destructive technique for analyzing the overlayer coverage of a 2D material directly on the growth substrate. A technique for determining the number of molecular layers using angle-resolved XPS has been developed. The system that will be presented is graphene growth on CuNi substrates, where controlled growth of multilayer graphene films can be performed. Since single atomic layer graphene films can be grown on Cu substrates, these samples are used as a standard reference for a monolayer of graphene. HOPG is used as a standard reference for bulk graphite. The electron mean free path of the C-

1s photoelectron can be determined by analyzing the areas under the C-1s peaks of monolayer graphene/Cu and bulk graphite. With the electron mean free path, the graphene coverage of a film of arbitrary thickness can be determined by analyzing the area under the C-1s of that sample. In principle, this technique can be used to determine the thickness of other 2D materials if a sample with a single molecular layer can be prepared.

AS-ThP10 Probing the Electrical Double Layer by *in situ* X-ray Photoelectron Spectroscopy through a Carbon Nanotube-Strengthened Graphene Window, *P. Wang, Yunfeng Li*, L.N. Wang, J. Klos, Z.W. Peng, N. Kim, University of Maryland, College Park; *H. Bluhm,* Lawrence Berkeley National Laboratory; *K.J. Gaskell, S.B. Lee, B. Eichhorn, Y.H. Wang,* University of Maryland, College Park

A detailed description of the electrical double layer structure formed at the electrode-electrolyte interface is very important for both fundamental understanding in many electrochemical processes and further advancements in energy storage devices. However, the electrical double layer is deeply "buried" by the bulk electrolyte solution, leading to significant signal loss and low detection resolution when measuring the interface structure from the electrolyte side. Here, we report the fabrication of a novel transparent electrode made of a graphene-carbon nanotube hybrid membrane that allows us to detect the electrical double layer from the solid side of the electrode using X-ray photoelectron spectroscopy. The robust and ultrathin nature of the hybrid membrane enables the detection of different elements with excellent photoelectron signals. By *in situ* monitoring the concentration changes of cations and anions under different local electrical potentials, we experimentally decipher the chemical structure of the electrical double layer, which is consistent with theoretical predictions.

AS-ThP11 Antibacterial Performance of Electrically Activated Conductive Water Filter Papers, *Dorina Mihut*, A. Afshar, L. Lackey, Mercer University

Silver and copper thin films were coated on commercially available 3 M water filter papers using DC high vacuum magnetron sputtering technique. The filter papers (10 X 7 cm size) are flexible structures consisting of nonconductive fibers and metallic nanoparticles were deposited with 300 nm and 1 μm thicknesses resulting in a complete coverage of the fibers surface. Both silver and copper thin films deposited on water filter paper are effectively working against common types of harmful bacteria that are found in waste water. The research is investigating the possibility of creating electrically conductive structures and the synergistic antibacterial effect obtained by using metallic thin films deposited on water filter paper and an electrical current applied to the structures. The antibacterial activity of electrically conductive structures was tested by applying an increased electrical potential. The morphology of the coatings and their adherence to the water filter paper was examined using the digital optical microscopy and Scanning Electron Microscopy and their chemical composition was investigated using the X-ray diffraction technique. A ll thin films showed good adhesion to water filter fibers and ensured a high area of exposure to contaminated water. The antibacterial effect of different conductive thin films was characterized by using the standardized membrane filtering technique for water and wastewater examination. The testing media (i.e. contaminated water) containing bacterial samples were collected from local wastewater basins. Water was tested for the bacterial content before and after the exposure to conductive thin films coated filters.

AS-ThP12 Biocompatible and Robust Non-wetting Surface Inspired by Three Natural Organisms: Lotus Leaf, Mussel, and Sandcastle Worm, *Kiduk Han*, POSTECH, Republic of Korea; *T.Y. Park,* POSTEC, Republic of Korea; *H.J. Cha, K. Yong,* POSTECH, Republic of Korea

When the contact angle of water to a specific surface exceeds 150°, the surface is referred to as superhydrophobic (SH) surface. This SH surface has been developed by mimicking the Lotus leaf structure and it is useful for preventing structural deformation, oxidation and contamination of materials that can be affected by water. However, the SH surface has a limitation in practical use due to its poor physical durability, and there has been a great difficulty in applying it to research fields such as medical and tissue engineering due to the biohazard of its components. To overcome these problems, we have developed a technique for producing biocompatible and robust SH surfaces using mussel adhesive-protein adhesive (iMglue), and have applied this technology to catheters and patches to confirm its biomedical utility. The nanoparticles were deposited on the iMglue by dip coating and spray coating method, and the surface energy of the particles was lowered through chemical reaction to produce a water repellent surface. This surface is expected to play an important role in biomedical field due to its antibacterial and wound closure capabilities.

AS-ThP13 In-situ ToF-SIMS Analysis of FIB Prepared Li Ion Battery Anodes, *Vincent Smentkowski, R. Hart, H. Cao,* GE-Research*; F. Kollmer, J. Zakel, H. Arlinghaus,* IONTOF GmbH, Germany

Depth profiling (1D or 3D) is often used to determine the depth distribution of species in a material. Depth profiling works well when the surface of a sample is smooth and when the depth(s) are in the nm to micron thickness range. For thicker layers, one can mount the material in epoxy and generate a cross section which can be imaged. Unfortunately, cutting and polishing often damages (or at least smears) fragile materials such Li ion batteries. Over the two past decades, Focused Ion Beam (FIB) has proven to be a viable approach to expose sub surface layers 10s of microns thick which is often analyzed by SEM or TEM in conjunction with EDS [1]. Unfortunately, most EDS detectors are not able to detect light species such as Li and C (especially at the degraded vacuum which most SEM's operate under), and definitely can not detect H. ToF-SIMS not only detects all elements (and their isotopes), it also allows for the analysis of molecular fragments which is often critical for understanding the material. FIB/ToF-SIMS has been used to analyze other material systems [2, 3].

In this late breaking poster, we will provide preliminary in-situ FIB/ToF-SIMS results which were generated on an anode taken from a Li ion battery. In order to simultaneously obtain high lateral resolution images at high mass resolution, the delayed extraction data collection mode was utilized [4]. The advantages of multivariate statistical analysis (MVSA) for these complex data sets will be demonstrated.

[1] Lucille A. Giannuzzi, and Fred A. Stevie, Eds., "Introduction to Focused Ion Beams", Springer-Verlag US (2005) DOI: https://doi.org/10.1007/b101190.

[2] Felix Kollmer, D. Rading, R. Moellers, H.-G. Cramer, Wolfgang Paul, Ewald Niehuis, "Novel Cluster Ion Beams For Secondary Ion Generation, Sputtering And FIB/SIMS Application", Microscopy and Microanalysis 18(S2) (2012) 904-905; DOI: 10.1017/S143192761200637X.

[3] John S. Hammond, Gregory L. Fisher, Scott R. Bryan, Rait Kanarbik and Pritt Möller "FIB-TOF Tomography of Solid Oxide Fuel Cells", Microscopy and Microanalysis 19 (suppl 2) (2013) 672-673, DOI:10.1017/S1431927613005357.

[4] Quentin P. Vanbellingen, Nicolas Elie, Michael J. Eller, Serge Della-Negra, David Touboul, Alain Brunelle, "Time-of-flight secondary ion mass spectrometry imaging of biological samples with delayed extraction for high mass and high spatial resolutions" Rapid Commun. Mass Spectrom. 29 (2015) 1187–1195, DOI: 10.1002/rcm.7210

AS-ThP14 Characterization of Surface-Immobilized Aptamers for Electrochemical Biosensing, *Ramya Vishnubhotla,* National Institute of Sandards and Technology (NIST)*; S.M. Robinson, J.P. Giddens,* University of Maryland, College Park*; S. Semancik,* National Institute of Standards and Technology (NIST)

Electrochemical measurements have shown promise for detecting biomolecules such as DNA and proteins. In this presentation, we focus on surface-immobilized DNA aptamers that can be used to bind certain species and thereby produce electrochemical signals indicating detection of desired targets. Our sensing approach is based on monitoring binding events and conformation changes that occur on reusable, temperature-controlled electrochemical microdevices. We present our findings on two "model" aptamers that bind streptavidin and platelet-derived growth factor (PDGF), respectively. The commercially-purchased aptamers were bound to the Au working electrodes of the devices through a thiol group that was synthesized at the 5' end of the DNA. Changes in temperature caused folding and unfolding of the aptamer, altering the average distance between a terminal redox-active methylene blue moiety (at the 3' end) and the Au surface. The resulting change in current (due to electron transfer between each methylene blue molecule and the Au surface) was monitored over a temperature range of ~10 ℃ – 60 ℃. Initial studies included surface characterization using XPS and AFM in order to better understand the behavior of the aptamers under environmental stressing, such as changes in the chemical environment and temperature. Surface plasmon resonance (SPR) studies were also performed to provide instrumental analyses of the aptamer-protein binding events, to compare to results obtained with the electrochemical microdevices.

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